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On the Question of the Constancy of the Cosmic Radiation and the Relation of these Rays to Meteorology – – – – – – – – – – – – – – ROBERT A. MILLIKAN 1585

On the Electrical Resistance of Contacts between Solid Conductors – – – J. FRENKEL 1604

X-Ray Absorption in Gases – – – – – – – – – – – – W. W. COLVERT 1619

Diffraction of X-Rays in Liquids: Effect of Temperature – – – – E. W. SKINNER 1625

On the Fluorescence of Quartz Under the Influence of Cathode Rays of Low Voltage – – – – – – – – – – – – – – – – – HEINRICH PETERS 1631

Pressure and High Velocity Vapour Jets at Cathodes of a Mercury Vacuum Arc – E. KOBEL 1636

Photoelectric Emission from Thin Films of Caesium – – – – – – L. R. KOLLER 1639

Magnetic Susceptibility of Gases. II. Temperature Dependence – – FRANCIS BITTER 1648

Magnetic Properties of Certain Pt-Co and Pd-Co Alloys – – F. WOODRIDGE CONSTANT 1656

Magnetic Isotropy of a Paramagnetic Alum – – – – – – – C. G. MONTGOMERY 1662

A Method for Growing Large Crystals of the Alkali Halides – – – JOHN STRONG 1663

Letters to the Editor – – – – – – – – – – – – – – – – – – 1667

Use of the Pierce Acoustic Interferometer, *W. H. Pielemeier*—1667; Wave Mechanics of Deflected Electrons, *E. H. Kennard*—1667; Simple Isotopic Constitution of Caesium, *K. T. Bainbridge*—1668; Problems in Acoustic Interferometry with Gases, *J. C. Hubbard*—1668; Magnetostriction and Magnetic Hysteresis, *L. W. McKeehan*—1670; Note on the Source of Dielectric Polarization, *Ralph D. Bennett*—1670; A Diophantine Equation Connected with the Hydrogen Spectrum, *T. H. Gronwall*—1671.

Book Reviews – 1673

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THE
PHYSICAL REVIEW

ON THE QUESTION OF THE CONSTANCY OF THE COSMIC RADIATION AND THE RELATION OF THESE RAYS TO METEOROLOGY

By Robert A. Millikan
California Institute of Technology
(Received October 23, 1930)

Abstract

Mean cosmic-ray intensities have been measured with much precision both at Pasadena, California (latitude 34) and at Churchill, Manitoba (latitude 59), the latter a distance of 730 miles from the North magnetic pole.

(1) The observed equality in these intensities indicates that these rays enter the earth's atmosphere as photons rather than as streams of electrons.

(2) Evidence is presented that the incoming rays are of a uniform intensity in all directions and in all latitudes, the small and apparently erratic fluctuations found by many observers at different stations arising simply from eruptions, waves, or ripples which change the thickness of the atmospheric blanket interposed between the source and the observer.

(3) The cosmic-ray electroscope thus acquires significance as a meteorological instrument.

(4) The influence of these rays in the maintenance of the earth's charge is considered.

I. Lack of Dependence upon Latitude

IN OUR trip to the Bolivian High Andes in 1926 Dr. Cameron and I, by taking continuous observations at sea from latitude 34 north to latitude 17 south, and also by observing at altitudes of about 15,000 feet both in California and in South America, proved to our own satisfaction that the cosmic-ray intensities are the same the world over at a given elevation above sea level, and also that they are independent of the positions of any celestial objects *within the limits of our experimental uncertainty*, which we estimated at about 3 percent but which in our report[1] we gave as 6 percent so as to have a sufficient margin of safety. This result has been questioned by other observers, and theories have been advanced which required a variation of cosmic-ray intensities both with latitude and with the positions of celestial objects, and I myself have thought it entirely possible that there might be small variations depending upon these elements. It was therefore very important for the theory of the origin of these rays to have much more exact measurements upon these points than we had yet made.

Having now an electroscope which by virtue of carrying a pressure of

[1] Millikan and Cameron, Phys. Rev. **31**, 170 (1928).

450 pounds of air per square inch, and by virtue of other improvements in construction is fourteen times as sensitive as the one used in South America—it has not leaked a particle of air for more than two years—I have within the past fifteen months returned to the problem of studying variations with both latitude and sidereal time, since it is one of altogether fundamental importance for the understanding of the nature of these strange rays.

From the first we ourselves have thought the evidence satisfactory that these rays are ether waves of frequencies a thousand times and more those of the hardest x-rays, but others have thought that they might not be ether waves at all, but high-speed electrons instead.[2] If they were the latter, they would of necessity be influenced by the earth's magnetic field and should be stronger near the magnetic pole than at low latitudes, as is the case with other phenomena, such as the aurora, which depend upon the earth's magnetic field.

This summer I therefore went to the settlement which is much the nearest to the earth's north magnetic pole of any settlement on earth, namely, Churchill, 730 miles due south of the pole on the west side of Hudson's Bay—at present a construction camp where the Canadian Government is trying to make a three months summer harbor for the sake of bringing Manitoba and Alberta closer to Liverpool. It is estimated, for example, that eight cents a bushel can thus be saved on the transport of wheat from northwestern Canada to England. A construction train runs into Churchill once a week, crawling along at about 20 miles per hour over tracks laid partially on frozen swamps.

There, through the extreme courtesy of the Carter-Halls-Aldinger Engineering Co. Ltd., and also with transportation assistance for my 500 pounds of lead and other baggage from the Southern Pacific, the Canadian Pacific, and the Canadian National Railroads, I took observations continuously day and night for a week on the intensity of the cosmic rays, screening out the local rays with this shield of lead 7.6 cm (about 3 inches) thick. The aurora played brilliantly overhead on three of the six nights of observation, so that if cosmic rays and the aurora are phenomena that are in any way connected, the opportunity for bringing to light that connection could not have been better. The mean results, when compared with those similarly taken at Pasadena during the last week in July and the first in August show that *the cosmic rays have precisely the same intensity at Churchill, in latitude 59, as at Pasadena in latitude 34*, the mean results in the two places being 28.31 ions per cc per sec. and 28.30 ions per cc per sec., respectively, as measured in my particular electroscope. I think the error in these measurements cannot possibly be as much as 1 percent.

Table I gives the actual readings taken at six hour intervals, the rate of discharge in ions per cc per sec. during the six hours from midnight to 6 A.M. being labelled "night," that from 6 A.M. to noon being labelled "morning," that from noon to 6 P.M. being called "afternoon," and that from 6 P.M. to midnight "evening."

[2] Bothe and Kolhörster, Zeits. f. Physik **56**, 751 (1929).

TABLE I. *Comparison of cosmic ray intensitis at Pasadena, California, latitude 34, and Churchill, Manitoba, Latitude 59.*

Pasadena, July 26 to August 3, 1930

	Night		*Morning*		*Afternoon*		*Evening*	
	Ions cc/sec	Barometer inches	Ions cc/sec	Barometer inches	Ions cc/sec	Barometer inches	Ions cc/sec	Barometer inches
	29.77	29.13	29.19	29.14	29.96	29.10	30.08	29.09
	29.10	29.08	29.42	29.16	29.98	29.15	29.65	29.16
	29.27	29.19	29.49	29.18	29.70	29.15	29.33	29.12
	29.37	29.14	29.46	29.14	30.23	29.10	29.58	29.11
	29.56	29.16	29.22	29.16	29.52	29.13	30.24	29.13
	29.68	29.12	28.93	21.12	30.00	29.08	30.16	29.06
	29.42	29.09	29.52	29.10	29.56	29.09	29.94	29.11
	29.35	29.14	29.21	29.18	29.07	29.18	29.28	29.17
Means	29.44	29.13	29.31	29.15	29.75	29.12	29.76	29.12

Mean Ions cc/sec = 29.56 Mean barometer = 29.13.401 Corrected bar. = 29.14
Correction for local rays = 52.5 × 2.4% = 1.26. ∴ Mean *I* cc/sec = 29.56 − 1.26 = 28.30 at mean barometer = 29.14.

Churchill, August 25 to September 1

	Night		*Morning*		*Afternoon*		*Evening*	
	Ions cc/sec	Barometer inches	Ions cc/sec	Barometer inches	Ions cc/sec	Barometer inches	Ions cc/sec	Barometer inches
	28.33	29.54	28.40	29.42	28.72	29.41	28.30	29.44
	28.24	29.49	27.88	29.58	28.46	29.66	28.53	29.77
	28.69	29.79	28.12	29.79	28.38	29.72	28.80	29.59
	27.82	29.47	29.10	29.35	29.17	29.27	29.25	29.26
	28.83	29.30	28.18	29.35			28.89	29.41
	28.57	29.45	27.63	29.51	28.06	29.61	28.39	29.63
	28.60	29.52	28.13	29.57	28.81	29.46		
Means	28.44	29.51	28.21	29.51	28.60	29.52	28.69	29.51

Mean ions cc/sec = 28.48 Mean barometer = 29.51 − 0.07 Corrected bar. = 29.44
Correction for local rays = 24. × 2.4 = .58. ∴ Mean *I* cc/sec = 28.48 − .58 = 27.90
Churchill ions cc/sec reduced to Pasadena barometer = 27.90 + 0.41 = 28.31
To compare with Pasadena observations 28.30

It will be noticed that the rays producing the observed 29 ions per cc per sec. inside the lead are almost pure cosmic rays, since the local rays amount to but 4 percent of the total at Pasadena and to less than 2 percent of the total at Churchill. The exact amount of the local rays in each position was determined by taking a reading without the lead screen and subtracting from this reading the cosmic-ray intensity as read off for the given elevation from our depth-ionization curve taken in snow-fed lakes with this same electroscope. The percentage of these local rays getting through the lead screen was found by making preliminary direct measurements with standard samples of uranium and thorium. It thus found that 2.4 percent of the local rays appear inside the lead. The zero of this electroscope, i.e., the reading when entirely screened from all rays, was 1.2 ions cc/sec, so that at Pasadena, for example, it was found that 27.1 out of the observed 29.56 ions per cc/sec were due solely to the cosmic rays. The recorded barometer readings are the means of those directly observed on my "precision Paulin" aneroid at the beginning and end of each run, and the indicated corrections were furnished me by the weather bureau stations at both Los Angeles and Churchill as read on their standard mercury barometers.

Since the portion of the sky from which the rays come at Churchill is quite different from that at Pasadena, the indications of these experiments are, then, First, *that the cosmic rays enter the earth uniformly from all portions of the sky*; Second, *that they consist as they enter the earth's atmosphere of ether waves, not of electrons.*

II. Lack of Dependence upon the Position of Andromeda or the Milky Way

But there are even more important conclusions than the foregoing that follow from the work thus far reported when it is taken in conjunction with the further experiments to be now considered.

When Dr. Cameron and I in 1925 proved[3] that the difference in the intensities of the cosmic rays at two levels in the atmosphere could be computed from the thickness of the blanket of air interposed between the two levels it of course followed that the intensity of the rays at the earth's surface must vary with barometric pressures, since these simply reflect approximately the varying weights of the atmosphere above. So when we had completed, more than a year ago, the full curve showing the variation of intensity with depth beneath the surface of the atmosphere, and could thus, with the aid of this curve, reduce the readings taken over days, or weeks, or months, to a common barometer-reading, I expected that the variability in the measured cosmic-ray intensities would disappear under this procedure. But continuous readings taken every six hours with very delicate instruments a year ago last summer seemed to spoil this expectation. They still showed fluctuations after careful reduction to a common barometer-reading, and for a while I thought these fluctuations came at such a time of day as to indicate that the Milky Way exerted a small positive influence upon the intensities of the rays. Although I mentioned to some of my colleagues my apparent finding that the Milky Way might increase the intensity of the rays by perhaps a percent by its presence overhead, I made no publication of even such a small dependence of cosmic-ray intensity upon stellar-time, for I wished first to extend the observations to different times of the year when the Milky Way would be overhead at widely different times of day.

Such a prolonged and continuous following of the changes has now brought to light the fact that neither the Milky Way or the nearest of the spiral nebulae Andromeda, nor any other celestial object has anything to do with these changes, but rather that they are a diurnal affair occurring at the same time of day at widely different seasons of the year and having a connection with the diurnal barometric cycle. It is well known that this diurnal cycle carries the barometer—especially in warm regions free from summer storms—through a minimum late every afternoon and a maximum in the morning. The cosmic-ray intensities at Pasadena go through a *maximum every afternoon* and a *minimum every morning* even after corrections have been made to bring the readings to a common pressure. Table II exhibits these facts clearly, the readings from July 14–19 are entirely consistent with

[3] Millikan and Cameron, Phys. Rev. **5**, 851 (1926).

TABLE II. *Cosmic ray intensities.*

July 14 to 19, 1930	Night		Morning		Afternoon		Evening	
	12:08–8:52	29.81	9:11– 1:08	30.07	1:20–6:10	30.14	5:18–11:52	30.21
	12:07–7:47	29.69	8:00– 2:02	29.33	2:13–6:06	30.16	6:24–11:56	29.53
	12:30–8:12	29.62	8:22–12:25	29.77	12:33–4:22	31.15	6:20–12:15	29.87
	11:40–6:03	29.61	6:13–11:06	29.85	11:17–3:41	29.77	4:31–11:25	30.03
	10:26–1:44	29.94	9:31– 1:57	29.62	2:07–6:20	30.77	3:52–10:16	29.83
	1:53–9:22	29.63						
Means		29.71		29.73		30.39		29.89
	Milky Way overhead all this period		Milky Way overhead most of this time		Milky Way entirely out of sight		Milky Way partially overhead	

July 19 to 27, 1930	Night		Morning		Afternoon		Evening	
	12:38–6:39	29.78	6:40–12:20	29.72	12:32–6:02	30.01	6:30–12:24	29.53
	12:32–6:02	29.43	6:19–12:32	29.67	12:43–6:18	30.08	6:14–12:16	29.99
	12:40–6:45	29.85	7:08–12:38	29.72	12:48–6:26	29.82	6:28–12:26	30.09
	12:28–6:39	29.99	6:58– 1:22	30.12	1:53–6:32	30.69	6:36–12:06	30.04
	12:19–6:45	29.93	6:55–12:29	29.91	12:38–6:34	30.13	6:43–12:07	30.42
	12:33–6:41	29.42	6:57–12:32	29.75	12:42–6:33	30.35	6:46–12:22	30.35
	12:11–6:22	30.10	6:33–12:44	29.57	12:55–6:30	30.26	6:44–11:58	30.22
	12:03–5:57	29.43	6:09–11:55	29.78	12:05–6:05	30.35	6:44–11:50	30.35
Means		29.74		29.78		30.21		30.12
	Milky Way overhead all this period		Milky Way overhead most of this time		Milky Way entirely out of sight		Milky Way partially overhead	

Oct. 6 to 12, 1929	Night		Morning		Afternoon		Evening	
Date								
10/6/29	11:56–8:05	30.09	8:25– 2:14	30.01	2:22–6:49	30.77	6:54– 1:04	30.52
10/7/29	1:11–10:24	30.30			10:33–6:22	30.53	6:30–11:40	30.65
10/8/29	11:52–8:12	20.21	8:13– 1:47	30.08	1:57–7:07	30.54	7:16–12:21	30.34
10/9/29	12:30–9:04	29.61	9:19– 2:15	29.90	2:26–6:50	30.63	6:59–11:69	30.20
10/10/29	12:07–9:10	29.88	9:21– 3:30	30.37	3:40–7:00	30.54	7:10–11:51	30.30
10/11/29	12:04–8:57	29.84	9:09– 2:04	29.73	2:15–6:20	30.80	6:29–11:57	30.24
10/12/29	12:10–9:09	29.92	9:21– 2:22	30.32				
Means		29.98		30.07		30.63		30.37
	Milky Way overhead most of this time		Milky Way entirely out of sight		Milky Way partially overhead		Milky Way overhead all this period	

those taken from July 19–27, the "night" readings and the "morning" readings being in both cases lower than the "afternoon" and "evening" readings. Further, the night readings are the most consistent among themselves because the atmosphere is then in its most quiet condition. As indicated two-thirds of the way down the table the Milky Way was here entirely out of sight *when the cosmic ray intensities were at their afternoon maximum.* I at first thought that this must mean that the Milky Way, instead of exerting a positive influence as had been before suspected must instead act as an absorbing screen for the cosmic rays. But, as shown at the bottom of the table, in October 1929 I had taken a similar series of readings. The Milky Way had then moved forward about 6 hours, so that it was completely out of sight in the *morning* instead of the afternoon, *and yet the relation of the morning and afternoon readings had not been altered a particle by this fact.* That the readings are all a little higher in October, 1929, than in July, 1930, has no significance save that I was reducing to a different barometer reading at the former time. Table II yields quite exact and unambiguous proof, then, *that the Milky Way has no influence whatever, and therefore that the cosmic rays must originate "in the depths of space beyond the Milky Way."*

Table III shows again the same relations. The day was here divided into seven periods instead of into four, the time at the top of each column being merely the median clock-reading for the period. Here too, it is seen that the maximum is in the late afternoon and the minimum at night or in the early morning.

TABLE III. *Cosmic ray intensities.* (Observations August 1 to August 9, 1930).

12:40 P.M.		3:30 P.M.		6:15 P.M.		9:45 P.M.	
10:22–4:05	29.45	1:20–6:51	29.99	3:34–8:21	30.42	6:14–12:00	30.00
10:07–3:25	30.20	12:46–6:35	29.79	3:25–9:19	30.05	7:00–12:45	29.60
10:01–3:17	29.72	12:57–6:45	30.07	4:00–9:29	29.85	6:33–12:27	29.81
10:23–3:23	29.67	12:43–6:14	29.75	4:13–9:30	29.65	6:56–12:56	30.24
10:35–4:40	29.50	12:57–3:50	29.85	4:07–9:53	30.05	6:22–10:40	29.97
10:06–2:29	30.01			3:33–7:58	30.56	8:32–12:42	29.87
11:11–3:57	29.83			3:28–8:29	30.09	7:25–11:55	30.49
9:56–3:25	29.90			3:21–8:00	29.93	8:36–12:30	29.40
				2:47–7:53	29.57	8:11–12:22	29.80
Means	29.79		29.89		30.02		29.91
Milky Way a little in		Milky Way nearly out		Milky Way entirely out		Milky Way out	

3 A.M.		7:45 A.M.		9:45 A.M.	
12:11–6:28	29.69	5:53–11:03	29.95	6:33– 1:05	29.89
12:55–6:43	29.66	5:34–10:16	29.52	6:50–12:48	29.73
12:42–6:36	29.86	5:25–10:25	29.72	6:47–12:35	29.55
11:50–5:47	29.91	5:10– 9:51	29.69	7:04–12:35	29.64
1:03–6:53	29.52	5:59– 9:57	29.62	6:09–11:56	29.79
10:51–5:12	29.65	4:32– 9:46	29.75		
9:43–3:36	29.62	4:10– 9:54	29.46		
12:53–6:45	29.50	3:47– 9:16	29.56		
7:45–3:53	29.51				
12:09–5:47	29.90				
12:41–6:55	29.89				
12:39–5:24	29.20				
12:32–5:13	29.98				
12:38–5:10	30.07				
Means	29.71		29.66		29.72
Milky Way in		Milky Way in full		Milky Way mostly in	

The sort of consistency and precision in electroscope readings here attained is rather nicely shown by Tables II and III, which reveal that in three different sets of observations taken over three different groups of days the three "night" mean-readings were 29.71, 29.74, and 29.71, while the three morning mean readings were 29.73, 29.78, 29.72. The afternoon and evening readings fluctuate more because the atmosphere is then more disturbed.

III. EXPLANATION OF FLUCTUATIONS

The reason for the behavior shown in Tables II and III is now quite clear. As the sun rises and begins to heat the earth the barometer begins to rise, not at first because there is any larger weight of atmosphere above it, but solely because the temperature of the air, partially confined by its viscosity and inertia, is rising. Before night the column of air over the heated area has expanded upward, flowed over at the top, and left a miniature terrestrial "sun spot" or hole in the atmosphere through which the cosmic rays then reach the earth in greater intensity merely because the air-blanket has been partially removed locally by the heated spot.

In a word, the barometer is an instrument that responds both to the *temperature* and to the *weight* of the superincumbent air, i.e., to a mixture of static and kinetic conditions, while the cosmic-ray electroscope reflects only the *mass* of the superincumbent air, and is quite independent of temperature, or of kinetic effects of any kind. *The cosmic-ray electroscope is thus a simpler and a more fundamental instrument than the barometer.* I expect it to be an aid in bringing about advances in the as yet little developed science of meteorology, and ultimately to find a place in meteorological stations. The air is simply an absorbing blanket interposed between us and a constant

source of radiation coming into the earth uniformly from all directions. Every eruption, or wave, or ripple in that blanket is accurately reflected by the cosmic-ray electroscope of the type here used. The changes that it reveals are considerably larger than the changes revealed by the barometer, because it cares nothing about the temperature, but only about the mass of the interposed layer of air, while with the barometer a rise in temperature often masks the thinning of the air-blanket above. The two instruments between them furnish more information about the condition of the upper air than either one of them alone can do. The afternoon barometer minimum, corresponding to a mean drop of one-tenth inch of mercury, or one-third percent, may be accompanied by a cosmic ray rise of two percent, as Tables II and III show.

IV. Clearing up of Former Discrepancies

The fourth result to which I would call attention is that the proof that the cosmic rays that strike the atmosphere are all ether-waves, rather than a mixture of ether waves and high speed electrons, carries with it the conclusion that the rate of ionization within a vessel sent to the top of the atmosphere should not be a maximum at the top as we have heretofore assumed, but should pass through a maximum somewhere below the top. This removes the apparent contradiction between the early results of Hess and Kolhörster (1911–1914), who went up in manned balloons, and Bowen and myself (1922), who sent up recording electroscopes with pilot balloons to much higher altitudes. We obtained a very much smaller *mean* absorption coefficient than they did, and this is precisely what we should have done in view of this aforementioned maximum. This result also brings to light new evidence for the correctness of the interpretation made by Dr. Cameron and myself that the cosmic rays are due to the continuous formation "in the depths of space" of the common abundant elements helium, oxygen, silicon, and iron out of hydrogen; for, before these ether waves get into equilibrium with their train of secondary electrons they should show absorption coefficients of the same order of magnitude as, but *somewhat smaller than*, those computed for them by the Einstein equation, Aston curve, and the Klein-Nishina formula. This is exactly what they do show, and they show this departure least for the rays corresponding to the formation of helium, for which the difference is quite small, and most for those corresponding to the formation of iron. This, also, is exactly in accord with our observations, reported to the Academy at its fall meeting a year ago.

V. Cosmic Rays and Atmospheric Electricity

About forty percent of the ionization in the atmosphere at the earth's surface over the land is due to cosmic rays and sixty percent to the radioactive substances contained in the earth, but at the altitude of Pike's Peak (14100 feet) we have found the cosmic rays three times as intense as at sea level, and this checks roughly with Hess' and Kolhörster's observations made as early as 1911 to 1914. But at altitudes above say two thousand feet the influence of rays from the earth in producing atmospheric ionization has become negli-

gible, the cosmic rays alone being here effective, *so that practically the whole ionization of the atmosphere above its surface layer and below the great altitudes at which the Kennelly-Heaviside layer is found is due to the cosmic rays.* These rays must therefore exert a preponderating influence upon atmospheric electrical phenomena.

We have heretofore had considerable difficulty in finding a mechanism by which the earth can maintain its well-known negative charge,—a charge sufficient to produce a more or less constant potential gradient, near the surface, of some 100 volts per meter. The cosmic rays, by detaching negative electrons from the molecules of the atmosphere and hurling them with enormous energy into the earth, must contribute somewhat toward the maintenance of this gradient; but they are much too few in number, indeed, of an entirely wrong order of magnitude, to account for the observed effects. Indirectly, however, they assist greatly in maintaining the earth's charge, the mechanism being presumably somewhat as follows:

The ionization of the upper air by the ultraviolet light from the sun is undoubtedly very large, enormously larger than that due to cosmic rays, as is shown by the existence of the Kennelly-Heaviside layer. The result of this ionization, whatever its cause, ultraviolet light, cosmic rays, or what not, is to free, in the higher stretches of the atmosphere, the lightest possible gas, namely, an electron gas, about 1/50,000th the weight of nitrogen gas, and this, because of its extreme lightness and mobility, at once expands upward, or *tries to do so*, until stopped by the field that such expansion itself creates, the greater chance of attachment of the electrons that diffuse downward accentuating this process. This field is of course of such sign as to tend to drive all the negative ions formed within it, and especially the attached negatives which have no tendency to diffuse upward, in toward the earth, and to hold the positives in the air above them. In other words, the outermost layers of the atmosphere in view of this influence, should have an excess of negatives, the next lower layers an excess of positives, and below that there should be a layer in which negatives are again in excess.

Now, no one has gone far enough up to find the aforementioned outermost layer, but Wiegand[4] and Idrac[5] both report altitude observations in which the field drops from 100 volts per meter at the surface to nearly zero at 8 kilometers and then, in the region between 8 and 12 kilometers, rises in such a way as to indicate an excess of negatives, followed by an excess of positives between 12 and 19 kilometers, where the field has again dropped to zero.

Now water vapor is found up to 12 kilometers, and wherever below that it is rising, expanding and condensing on ions, it will condense, according to the C. T. R. Wilson effect, only on the negatives, although a droplet may afterward catch a positive by the diffusion process. Furthermore, atmospheric dust is usually found predominently negatively charged. Negative capture seems, then, to be *strongly* favored by the C. T. R. Wilson effect, and to be somewhat facilitated by the excess of negatives between 8 and 12

[4] Wiegand, Ann. d. Physik **66,** 261 (1921).
[5] Idrac, Comptes rendus **182,** 1634 (1926).

kilometers, and also by the greater tendency of negatives, due to greater mobility, to collect on dust. After such capture gravity of course pulls this negatively charged dust and water vapor into the earth.

This gravitational effect on heavy, negatively charged carriers is, then, what creates a portion at least, of the negative gradient near the surface, a field that actually decreases rapidly with altitude, and if this theory is correct, should be reversed at high altitudes. A "gravity" theory of the maintenance of the earth's charge is not at all new, though there may be some elements of novelty in the foregoing elaboration of it. The purpose here is to point out the very important role that the cosmic rays play in it, since they must furnish practically all the atmospheric ions between the thin layer next the earth and the Kennelly-Heaviside layer.

VI. Summary

In summary, then, we have presented convincing evidence

(1) That the cosmic-ray intensities are independent of latitude.

(2) That the cosmic-ray intensities are independent of sidereal time.

(3) That the rays are constant all over the earth's surface, but that the fluctuations observed by many experimenters merely reflect changes in the thickness of the interposed atmospheric blanket.

(4) That the cosmic-ray electroscope may be of use in meterology.

(5) That the cosmic rays enter the atmosphere as ether waves or photons, and hence produce their maximum ionization, not at the surface of the atmosphere, but somewhat farther down.

(6) That the observed cosmic-ray effects are all in all good general agreement with the predictions of the Klein-Nishina formula, thus lending support to the view that the cosmic rays are due to atomic synthesis going on "in the depths of space."

(7) That the cosmic rays are a very important factor in atmospheric electrical effects, especially in the maintenance of the earth's negative charge.

ON THE ELECTRICAL RESISTANCE OF CONTACTS BETWEEN SOLID CONDUCTORS

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Abstract

A contact between two solid conducting bodies is visualized as a small gap between them. This gap can be described as a potential-hill over which electrons, according to the wave-mechanical theory, can pass even with insufficient kinetic energy. The general expression of the resulting current intensity as function of the potential-difference is obtained and discussed for the case of two identical or different bodies in connection with the resistance of granular structures (thin metallic films) and the rectifying action of certain contacts.

Introduction

THE usual picture of an electrical contact between two solid conducting bodies is that their surfaces or part of their surfaces are at a distance of atomic dimensions from each other, so that the electrons can pass through the contact surface in the same way they pass through any surface within the same body.

Now such an intimate contact between two bodies along a large part of their surfaces is probably very rarely realized. Nor is it necessary for the conduction of electricity from one body to the other. Such conduction can also take place through those parts of their surfaces which lie rather far apart from each other, that is, at a distance many times larger than the usual atomic distance. In fact, according to a well-known principle of wave mechanics, which has been used already (and sometimes abused) for the explanation of a great many phenomena, an electron can jump over a "potential-hill" even if it does not have sufficient kinetic energy to do so according to the classical mechanics. Now the gap between two contiguous bodies may be considered as the top of such a hill, with practically vertical slopes at (or rather just beyond) the respective surfaces. There must be in general a steady flow of electrons across the gap in both directions, the difference between the two flows being the actually observed current intensity I. In the case of equilibrium the latter is of course equal to zero. If, however, an additional potential difference ϕ is maintained across the gap, I will be a certain function of ϕ, different from zero.

It will be our first object to determine the general character of this function $I(\phi)$. Before, however, proceeding further let us remark that this function can always be expanded in a power series and that for small values of ϕ one can simply put $I=\alpha_1\phi$ in accordance with Ohm's law, α_1, being the conductivity of the contact, that is the reciprocal of its electrical resistance. For larger values of ϕ one must get

$$I = \alpha_1\phi + \alpha_2\phi^2 + \alpha_3\phi^3 + \cdots .$$

The coefficients of the even powers of ϕ vanish in the case of a contact between two identical bodies. They must be however different from zero in the case of two bodies of different nature. One thus gets in this case, to the second approximation, $I=\alpha_1\phi+\alpha_2\phi^2$, which means that the current is changed in magnitude when the sign is reversed. This means a rectification effect of the same type as that given by an electron valve on the curved part of the characteristic, and may be quite large for some particular contacts.

1. General Theory

For the sake of simplicity we shall consider the contiguous surfaces of the two bodies (a, b) as two parallel infinite planes. Their distance apart will be denoted by δ. The potential energy curve will be represented by the full line $MNQRST$ (Fig. 1) $NQ=U_a$ and $SR=U_b$ denote the increase of potential energy of an electron crossing the surface of the respective body (from inside to the outside). The inclined line QR represents a homogeneous electrical field acting between the two bodies. The corresponding change of the potential energy of an electron passing across the gap from a to b will be denoted by V and will be reckoned positive if this energy is diminished (as shown on the figure), that is, if the force F acting on the electron in the gap is directed from a to b ($F=V/\delta$). In the following it will be always supposed that the potential energy of an electron in a is *higher* than in b; the difference represented by the line N_1S_1 will be denoted with U_{ab}. One has the obvious relation $U_b-U_{ab}+V=U_a$ or

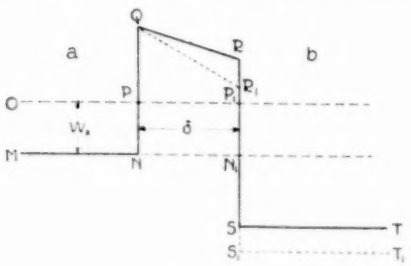

Fig. 1.

$$U_{ab} = U_b - U_a + V \tag{1}$$

$NP=W_x$ represents the kinetic energy of an arbitrarily selected electron in a, or rather that part of its kinetic energy W, which corresponds to the x-component of the velocity, the x-axis being drawn in the direction ab. *Every* electron in a for which this component v_x is positive, will be able to pass through the gap, no matter how small W_x is, in comparison with the height of the potential wall NQ. On the other hand only those electrons of b will be able to jump over the gap to a for which the part of the kinetic energy corresponding to the x-component of the velocity (in the negative direction) is larger than $SN_1=V$

The "transmission coefficient" for the a-electrons with the energy W_x will be denoted with $D(W_x)$. It is equal to the probability of any such electron passing from a to b (or the fraction of all the electrons succeeding in this enterprise). On the other side of the gap, that is in b, such an electron will have for the x-direction the kinetic energy W_x+U_{ab}. Reversing the direction of its motion we should get the same probability $D(W_x)$ for its getting back to a.[1] We thus see that $D(W_x)$ is the probability of a b-electron having for the negative x-direction the kinetic energy W_x+U_{ab}, to pass across the gap to a. The number of electrons per unit volume having velocity components in dv_x, dv_y, dv_z will be denoted by $f_a dv_x dv_y dv_z$ and $f_b dv_x dv_y dv_z$ for a and b respectively. So far as the *change in the velocity distribution of the electrons in each body*, due to the passage of the electrons to the other body or from the latter, can be neglected, f_a and f_b can be treated as functions of the resulting kinetic energy $W=W_x+W_y+W_z=\frac{1}{2}m(v_x^2+v_y^2+v_z^2)$. In case of two metals these are the well-known Fermi-Pauli-Sommerfeld functions.[2]

$$f_a = 2\left(\frac{m}{h}\right)^3 \frac{1}{e^{W/kT}/A+1}, \quad f_b = 2\left(\frac{m}{h}\right)^3 \frac{1}{e^{W/kT}/B+1}. \tag{2}$$

The number of electrons passing from a to b per unit surface per second is equal to

$$I_1 = \int_0^\infty dv_x \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dv_y dv_z D(W_x) f_a v_x.$$

For the corresponding number of electrons passing from b to a we get

$$I_2 = \int_{v_x{}^0}^\infty dv_x \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dv_y dv_z D(W_x - U_{ab}) f_b v_x.$$

Where $v_x{}^0$ is defined by the condition $\frac{1}{2}m(v_x{}^0)^2 = U_{ab}$. These expressions may be simplified by introducing instead of v_x the variable $W_x=\frac{1}{2}mv_x{}^2$ and instead of v_y and v_z the variable $R=W_y+W_z=\frac{1}{2}m(v_y{}^2+v_z{}^2)$ and the angle $\phi=\arctan(v_y/v_z)$. It will be remarked that $(2R/m)^{\frac{1}{2}}$ and ϕ are the polar coordinates replacing the rectangular coordinates v_y, v_z. We get then

$$I_1 = \frac{2\pi}{m^2} \int_0^\infty dW_x D(W_x) \int_0^\infty f_a(W_x + R) dR \tag{3}$$

and

$$I_2 = \frac{2\pi}{m^2} \int_{W_x{}^0}^\infty dW_x D(W_x - U_{ab}) \int_0^\infty f_b(W_x + R) dR$$

or replacing W_x by $W_x{}^1 = W_x - U_{ab}$,

$$I_2 = \frac{2\pi}{m^2} \int_0^\infty dW_x{}' D(W_x') \int_0^\infty f_b(W_x{}' + U_{ab} + R) dR. \tag{4}$$

[1] Cf. J. Frenkel, Einführung in die Wellenmechanik, p. 57.

[2] Cf. A. Sommerfeld, Zeits. f. Physik **47**, 7 (1928).

The resulting flow of electrons from a to b is

$$I = I_1 - I_2 = \frac{2\pi}{m^2}\int_0^\infty dW_z D(W_z) \int_0^\infty [f_a(W_z + R) - f_b(W_z + U_{ab} + R)]dR. \quad (5)$$

We shall now suppose that $I=0$. This means that the two bodies are in a statistical equilibrium with respect to each other, as a result of the existence of a definite contact potential difference between them, corresponding to the drop of potential energy V in the gap.

This state of equilibrium must obviously be independent of the special shape of the function $D(W_z)$, which determines the velocity with which it is established or the time of relaxation. Therefore in the case of equilibrium the coefficient of $D(W_z)$, that is the integral over R in (5), must vanish for any value of W_z, whence it follows that the integrand must vanish. We get thus, as the condition of equilibrium

$$f_a(W) = f_b(W + U_{ab}) \quad (6)$$

This equation can be considered as the direct consequence of the principle of detailed balance.

Let us now assume that V is increased by the amount V_1, corresponding to an additional (external) potential difference $\phi = V_1/e$ (e = charge of an electron). Instead of the initial potential energy curve Fig. 1, we shall get in this case the curve $MNQR_1S_1T_1$ (partially dotted line) if V_1 is positive (which it, of course, need not be). This will alter to some extent the transmission coefficient $D(W_z)$ replacing it by $D_1(W_z)$ say, and what is more important, change the potential energy difference U_{ab} replacing it by $U_{ab}+V_1$. As a result I_2 will now be smaller than I_1 (if $V_1>0$), and we shall have a current flowing through the gap in the direction of the applied electrical force. Taking account of the condition (6) we can determine this current by the formula

$$I = \frac{2\pi}{m^2}\int_0^\infty dW_z D_1(W_z) \int_0^\infty [f_b(W_z + U_{ab} + R) - f_b(W_z + U_{ab} + V_1 + R)]dR \quad (7)$$

For sufficiently small values of V_1, we can put

$$f_b(W_z + U_{ab} + R) - f_b(W_z + U_{ab} + R + V_1) = -V_1\frac{\partial f_b(W_z + U_{ab} + R)}{\partial R}.$$

This reduces the inner integral in (7), in view of $f_b(\infty)=0$ to $V_1 f_b(W_z+U_{ab})$, so that neglecting the difference between D and D_1, which is immaterial so far as second powers of V_1 are neglected, we get to a first approximation

$$\frac{I}{V_1} = \frac{2\pi}{m^2}\int_0^\infty dW_z D(W_z) f_b(W_z + U_{ab}) \equiv \alpha_1. \quad (8)$$

This expression, or rather its product with e^2, may be defined as the reciprocal of the resistance of the contact (per unit surface). Putting $V_1 = eE\delta$ where E is the (additional) electrical field in the gap, we can define the quantity

$$\frac{eI}{E} = \frac{e^2 I\delta}{V_1} \equiv \sigma_g$$

that is

$$\sigma_g = \frac{2\pi e^2\delta}{m^2}\int_0^\infty dW_x D(W_x) f_b(W_x + U_{ab}) \tag{9}$$

as the specific "conductivity" of the gap forming the contact.

Proceeding to the second approximation, we get

$$f_b(W_x + U_{ab} + R) - f_b(W_x + U_{ab} + R + V_1) = -V_1\frac{\partial f_b}{\partial R} - \frac{V_1^2}{2}\frac{\partial^2 f_b}{\partial R^2}$$

$$D_1 = D + \frac{\partial D}{\partial V_1}V_1$$

(the arguments being in both cases those corresponding to $V_1 = 0$) whence

$$I = \alpha_1 V_1 + \alpha_2 V_1^2 \tag{10}$$

with the previous value of α_1 and

$$\alpha_2 = \frac{2\pi}{m^2}\int_0^\infty dW_x\left[\frac{1}{2}D(W_x) f_b'(W_x + U_{ab}) + \frac{\partial D}{\partial V_1} f_b(W_x + U_{ab})\right] \tag{11}$$

f_b' denoting the first derivative of f_b.

It must be emphasized that the above results hold for the case only that $U_{ab} + V_1$ remains positive. If $U_{ab} + V_1 < 0$ the role of the bodies a and b will be exchanged.

2. Application to the Case of Two Identical Metals and to Granular Structures (thin films)

The last remark applies in particular to the case of a contact between two identical metals, which is characterized by U_{ab} (as well as V) being equal to zero. The second term in (10) will then vanish, and I will be an odd function of V_1.

Introducing f for f_b in one of the expressions (2) we get in this case for the "specific conductivity" of the gap

$$\sigma_g = \frac{4\pi m e^2\delta}{h^3}\int_0^\infty dW_x \frac{D(W_x)}{e^{W_x/kT}/A + 1}. \tag{12}$$

It will be interesting to compare this expression with that of the usual specific conductivity of the corresponding metal σ as derived from Sommerfeld's theory. The latter expression can be put in the form

$$\sigma = \frac{e^2 ln}{mv_0} \tag{13}$$

where n denotes the number of electrons in unit volume, v_0 their maximum velocity for $T=0$, and l the mean free path of the electrons having this velocity.[3] Putting

$$n = 2\left(\frac{m}{h}\right)^3 \int\int\int_{-\infty}^{+\infty} \frac{dv_x dv_y dv_z}{e^{W/kT}/A + 1} = 8\pi\left(\frac{m}{h}\right)^3 \int_0^\infty \frac{v^2 dv}{e^{W/kT}/A + 1}$$

$$= \frac{8\pi m^2}{h^3} \int_0^\infty \frac{v dW}{e^{W/kT}/A + 1}$$

we see that the integral

$$\frac{8\pi m^2}{h^3} \int_0^\infty \frac{dW D(W)}{e^{W/kT}/A + 1} \tag{14}$$

can be considered as the mean value of $D(W)/v$ for all the electrons (irrespective of the direction of their velocity). We thus get, according to (12)

$$\sigma_g = \frac{1}{2} \frac{e^2 \delta n}{m} \overline{\left(\frac{D}{v}\right)} \tag{15}$$

or approximately—putting $\overline{(D/v)} = \bar{D}/v_0$

$$\frac{\sigma_g}{\sigma} = \frac{1}{2} \frac{\delta \bar{D}}{l} \tag{15a}$$

This relation shows, that with respect to its conductivity the gap can be treated as a metal, where the free electrons have a mean free path of the order of magnitude of $\delta\bar{D}$. One can of course use it in the opposite way and treat a metal as a series of gaps. This interpretation roughly corresponds to the theories of Bloch and Peierls, where the electrons are considered as bound to the separate atoms, but still capable of jumping from one atom to the next one over the potential hill separating them.

The transmission coefficient D in the case of two identical metals $U_a = U_b = U$, that is for an energy-curve of the shape shown by the full line line of Fig. 2, is given as a function of the energy $W_x = \frac{1}{2}mv_x^2$ so long as the

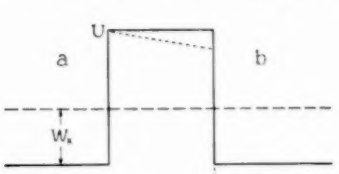

Fig. 2.

latter is smaller than U_0, by the formula

$$D = \left[\operatorname{csh}^2 \beta\delta + \frac{1}{4}\left(\frac{\beta^2}{\alpha^2} - \frac{\alpha^2}{\beta^2}\right)^2 \sinh^2 \beta\delta\right]^{-1} \tag{16}$$

[3] A. Sommerfeld, Zeits. f. Physik **47**, 1 (1928). Formulas (48c) and (42a).

where[4]

$$\alpha^2 = \frac{8\pi^2 m}{h^2} W_x, \quad \beta^2 = \frac{8\pi^2 m}{h^2}(U - W_x). \tag{16a}$$

For values of $\beta\delta$ which are large compared with 1, this reduces approximately to

$$D = 4e^{-2\beta\delta}\left[1 + \left(\frac{U}{2W_x}\,\frac{U - 2W_x}{U - W_x}\right)^2\right]^{-1}. \tag{17}$$

It may be convenient to write β in the form $\beta = 2\pi/\lambda$ where λ can be defined as the wave-length of an electron moving with the positive kinetic energy $U_0 - W_x$. If expressed in volts this energy is equal to ϕ, then

$$\lambda = \frac{1.1 \times 10^{-7}}{\phi^{1/2}} \text{ cm} = \frac{11}{\phi^{1/2}} \text{ Angstrom units.}$$

For the electrons with velocity $v_x = v_0$, that is, the maximum velocity at zero-point of temperature, which approximately corresponds to the maximum of the Fermi distribution curve in the region of usual temperatures, the difference $U_0 - W_x$ is just equal to the work function of the metal (as measured directly in the Richardson effect).[5] Putting $\phi \leqq 4$ volts we get for these electrons (using Angstrom units for λ and for the distance δ):

$$\lambda \leqq 5, \quad \beta \leqq 1.2, \quad 2\beta\delta \leqq 2.4\delta.$$

Since the expression in brackets in (17) is of the order of magnitude 1, we get as a rough estimate of the transmission coefficient D for $W_x = \frac{1}{2}mv_0^2$

$$D_0 \leqq e^{-2.4\delta}.$$

If the mean value of D entering in (15a) could be identified with D_0, we should have

$$\frac{\sigma_g}{\sigma} \leqq \frac{\delta}{l} e^{-2.4\delta}$$

that is for $\delta = 10A$ with $l \leqq 100$ (which roughly corresponds to the mean free path of the electrons at room temperature)

$$\sigma_g/\sigma \leqq 10^{-10}.$$

To get absolute figures we note that for good conductors the specific resistance $1/\sigma$ is of the order of 10^{-5} ohms. The resistance of the contact $r = \delta/\sigma_g$ reckoned per unit surface (in cm^2 of course) thus turns out to be of the order of $10^{-7} \cdot 10^5 = 10^{-2}$ ohms. For a twice larger gap with $\delta = 20A = 2 \times 10^{-7}$ cm we should get in the same way a resistance about 10^{10} times larger than the previous one, that is, about 10^8 ohms. Further increase of δ

[4] Cf. J. Frenkel, reference 1, p. 59.

[5] A. Sommerfeld, reference 3, formula (53b).

would mean practically complete disappearance of current; for with $\delta = 20A$ it would require an electric field of 10 million volts per cm across the gap, corresponding to a potential difference of 2 volts, to obtain a current of the order of 10^{-8} amp/cm^2.

It must be remarked that for such high values of the field intensity—or rather of the potential difference—the current would no longer be proportional to the latter, but would increase much faster, gradually assuming the character of Millikan's "field-currents." It can be easily shown that this character, corresponding to a practically unidirectional flow of electrons (from a to b, that is in the direction of the applied force only), would be acquired for potential differences of the same order of magnitude as that corresponding to the potential jump at the surface of the metal (U_a/e).

We must now come back and test the validity of our assumption that the mean value of the transmission coefficient $\overline{D(W_x)}$ can be identified with its value D_0 for the electrons with the velocity $v_x = v_0 (= v_{\max}$ for $T = 0)$.

To do this we must find out the maximum of the function

$$F(W) = \frac{D(W)}{e^{W/kT}/A + 1}$$

which enters the integral (14) defining the mean value of $D(W)/v$. Leaving aside the case of extremely high temperatures we can put $A = e^{-W_0/kT}$ where $W_0 = \frac{1}{2}mv_0^2$. Neglecting the variations of the denominator of (17) when compared with that of the numerator we can further put, according to (16a),[6]

$$D(W) \cong e^{-[(U-W_0)/kT_1]^{1/2}} \tag{18}$$

the "effective temperature" T_1, being defined by

$$1/kT_1 = 32\pi^2 m\delta^2/h^2. \tag{18a}$$

This gives

$$F(W) = \frac{e^{-[(U-W)/kT_1]^{1/2}}}{e^{(W-W_0)/kT} + 1}$$

or with

$$\frac{W_0}{kT} = \xi_0, \quad \frac{W}{kT} = \xi, \quad \frac{U}{kT} = \xi_1, \quad \frac{U-W}{kT_1} = \gamma(\xi_1 - \xi), \quad \gamma = \frac{T}{T_1}$$

$$F(W) = \frac{e^{-[\gamma(\xi_1-\xi)]^{1/2}}}{e^{\xi-\xi_0} + 1}. \tag{19}$$

The maximum of this function corresponds to the minimum of its reciprocal. Putting $\partial F^{-1}/\partial\xi = 0$ we get

$$1 + e^{-(\xi-\xi_0)} = 2[(\xi_1 - \xi)/\gamma]^{1/2}. \tag{19a}$$

It can be easily shown[7] that this equation has either two solutions $\xi = \xi' < \xi_0$ and $\xi = \xi'' > \xi_0$, or none, depending upon the value of the parameter γ. The

[6] This implies, of course the limitation to the case $W < U$, see below.

[7] For instance, graphically, by tracing the exponential curve $Y = 1 + e^{\xi-\xi_0}$ and one branch of the parabola $Y = 2[(\xi_1-\xi)/\gamma]^{1/2}$ (for $\xi < \xi_1$).

limiting value of this parameter is approximately equal to ξ_1. When $\gamma \gg \xi_1$, the equation (19a) has no solution, which means that the function (19) steadily increases, as ξ increases from 0 to ξ_1. In the opposite case $\gamma \ll \xi_1$, we get approximately

$$e^{\xi_0 - \xi'} \leqq 2\left[(\xi_1 - \xi_0)/\gamma\right]^{1/2} \text{ and } 2\left[(\xi_1 - \xi'')/\gamma\right]^{1/2} \leqq 1 \tag{20}$$

the first solution corresponding to a sharp maximum of $F(W)$ in the neighborhood of $W = W_0$, and the second to a faint minimum in the neighborhood of $W = W_1$. In order to see what case we have to deal with in practice, we must introduce numerical values.

If δ is measured in Angstroms, then it follows from (18a) $T_1 = 1.2 \times 10^4/\delta^2$ Thus the "effective temperature" is high for $\delta = 1A$ which means an actual contact between the two metals, of the order of magnitude of the room temperature = 120°K for $\delta = 10A$ and becomes very small as δ increases beyond this value.

Assuming U_a to be equivalent to 14 volts and W_0 to 10 volts, and taking $T = 300°\text{K}$, which corresponds with respect to the thermal energy kT to about 0.02 volts, we get $\xi_0 \leqq 500$ and $\xi_1 \leqq 700$.

We thus see, that in the above considered case of a gap $\delta = 10A$, the parameter γ is approximately equal to 2.5, that is, extremely small compared with its limiting value 700. For this case the first of the equations (20) gives approximately $\xi_0 - \xi' \leqq 20$ and the second $\xi_1 - \xi'' \leqq 2$. It can be easily verified that the maximum of $F(W)$ at $W = W' = kT\xi'$ is actually so sharp that $D(W)/v$ is practically equivalent to $D(W')/v'$ which is only very slightly different from the value $D(W_0)/v_0$ assumed above.

The condition $\gamma > \xi_1$ can be realized at $T = 300°\text{K}$ for very broad gaps only with a width $\delta > 170A$. In this case the main part of the electric current —*for sufficiently small values of the potential differences* $\phi = V_1/e$, that is, for very small field intensities $E = \phi/\delta$—should be due to electrons having a kinetic energy larger than U. For these electrons the transmission coefficient $D(W)$ is of the order 1, whereas their number for usual temperatures is extremely small. The electric current between a and b would have in this case the character of a thermionic current (and not of a field current) whose strength can be calculated by using the general expression (15a) for the effective conductivity of the gap with[8]

$$D \leqq e^{-(\xi_1 - \xi_0)} = e^{-(U - W_0)/kT}. \tag{21}$$

Thus in this case the electrical resistance of the gap $r = \delta/\sigma_g$ should be independent of its width δ and should vary with the temperature as $e^{-(u - W_0)/kT}$ It would have an appreciable magnitude only for very high temperatures lying in the same range as the temperatures for which thermionic currents are observed. For usual temperatures, gaps of such width could no longer be treated as contacts, whereas in the case of shorter gaps with $\delta \leqq 10\text{A}$ their resistance would be practically independent of the temperature and would vary exponentially with increase of δ.

[8] This being (approximately) the relative number of electrons with a kinetic energy larger than U.

The above results may have interesting applications to the question about the electrical resistance of granular structures, such as metallic powders and probably also extremely thin metallic films obtained by means of cathode sputtering. As well known, the latter possess an abnormally high specific resistance, which for films with a thickness of about 10^{-6} cm and lower, may be 20 times larger than that of the same metal in block, and further abnormally small temperature coefficient of resistance, which in fact can become negative (decrease of resistance with increase of temperature). It has been often assumed[9] that the high value of the specific resistance of very thin films is explained by the fact that their thickness may be smaller than the normal mean free path of the electrons (the latter being supposed to be scattered irregularly from both surfaces of the film). It would follow from this idea, that the "critical thickness" d for which the specific resistance should begin to increase, must be approximately equal to the mean free path l, and therefore must vary with the temperature in the same way as does the latter. According to the modern wave-mechanical theory of metallic conduction l varies inversely with T (or still faster in the region of very low temperatures), whereas as a matter of fact d remains practically independent of the temperature.

If on the other hand we adopt the equally often advocated granular theory of the constitution of thin films, and substitute for the usual conception of metallic contacts (which has been a serious obstacle for this theory) the conception developed in this paper, then the main properties of these films, distinguishing them from the metal in block, receive a satisfactory explanation. To say nothing of the abnormally high specific resistance, the smallness (or even the negative sign) of its temperature coefficient may be explained by the fact that the width of the gaps between adjacent grains is diminished, as a consequence of their thermal dilatation, with increase of temperature. Account should be taken of course of the thermal dilatation of the dielectric base upon which the film is deposited. But a comparison of the thermal dilation coefficients shows that they are as a rule larger in the case of the metals. This relation can be illustrated by the fact that the gaps between adjacent rails in a railway line decrease in the summer and increase in the winter time, and not vice versa. Denoting the length of a rail or grain with L and its effective dilation coefficient with α, we see that when the temperature is raised by ΔT the width of the gap is decreased by $\Delta\delta = -L\alpha\Delta T$. The relative decrease $\Delta\delta/\delta = -(L/\delta)\alpha\Delta T$ may be quite large even for a very small value of $\alpha(\leqq 10^{-5})$ if L is sufficiently large with respect to δ. And since the resistance of a gap varies exponentially with δ, this means a marked decrease of resistance, partially compensated by the normal increase of the resistance of the separate grains.

It is further well known that the resistance of thin films depends very largely upon the gas or gases present during their preparation. On our theory these gases must make thin monomolecular adsorbed layers on the surface of the separate grains of which the film is built up, thus changing

[9] An assumption that has been worked out mathematically by J. J. Thomson long ago.

the potential energy U which determines the transmission coefficient according to (18) and consequently the resistance of the gaps between the grains. It may be remarked that this change of resistance must be quite parallel to the change of the thermionic emission of the corresponding metal owing to the presence of the adsorbed layer. In fact the difference $U-W_0$ in equation (18) may be identified with the "work function" $U-W_0$ which determines the thermionic emission in Sommerfeld's theory. It follows then from (15a) that the logarithm of the specific conductivity of a gap (contact) must vary with U, as the square root of the logarithm of the thermionic emission of the same metal for the "effective" temperature.

3. Application to the Case of Two Different Conductors and to the Phenomenon of Rectification

Turning now to the consideration of a contact between two different conducting bodies (a, b) we shall first consider them as metals; the case of a non-metallic body (semi-conductor) may be obtained perhaps (see below) by taking the extreme form of the Fermi distribution law for a small concentration of free electrons which is nothing else but Maxwell's distribution law.

We have seen that when between two metals "in contact" that is at a small distance from each other, a potential difference V, determined by (1) and (6) is established, there will be no current flowing between them. Putting in (2) $A=e^{-W_a/kT}$ and $B=e^{-W_b/kT}$, we get, according to (6) $W-W_a=W-W_b+U_{ab}$ or according to (1).

$$V=(U_a-W_a)-(U_b-W_b). \tag{22}$$

This formula shows that the contact potential difference between two metals is equal to the difference of their respective work functions, as of course it should be.[10]

If a small additional potential difference V_1 is introduced, we must get a current determined by the "specific conductivity" (9). By the same argument as in the preceding paragraph we easily get

$$\sigma_g \leqq \frac{1}{2}\frac{e^2\delta n_b D(W_g)}{mv_g}$$

where $W_g+U_{ab}=W_b$, W_b being (practically) the maximum kinetic energy of of the electrons in the body b at $T=0$. Since, according to the equilibrium condition $W_b-U_{ab}=W_a$, we get further, dividing σ_g by $\sigma_b=e^2l_bn_b/mv_b$ the specific conductivity of the metal b,

$$\frac{\sigma_g}{\sigma_b} \leqq \frac{1}{2}\frac{\delta}{l_b}\frac{v_b}{v_a}D(W_a) \tag{23}$$

where $v_a=v_g$ is the largest velocity of the electrons in a at $T=0$. So far as v_a and v_b are of the same order of magnitude (which is the case for all metals)

[10] Cf. C. Eckart, Zeits. f. Physik **38** (1928) and J. Frenkel, Zeits. f. Physik (1928).

we do not have to discuss this expression in detail, since it is practically the same as in the case of two identical metals.

A few words should be added with regard to the character of the function $D(W_x)$.

For the case of the energy curve $MNQRST$ of Fig. 1 with an inclined top, this function cannot be evaluated in a simple way. We can, however, simplify the problem by replacing the inclined top line QR by a horizontal line $Q'R'$ passing through its center. We shall thus get a practically equivalent energy curve $MNQ'R'ST$ (Fig. 3), for which the function D is given

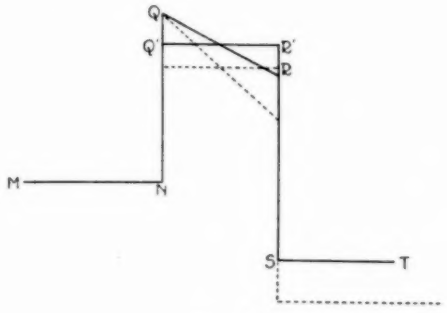

Fig. 3.

by the formula

$$D = \frac{4\alpha_a\alpha_b}{(\alpha_a+\alpha_b)^2 \operatorname{csh}^2\beta\delta + (\beta - \alpha_a\alpha_b/\beta)^2 \sinh^2\beta\delta}$$

where

$$\alpha_a^2 = \frac{8\pi^2 m}{h^2}W_x, \quad \alpha_b^2 = \frac{8\pi^2 m}{h^2}(W_x + U'), \quad \beta^2 = \frac{8\pi^2 m}{h^2}(U_a' - W_x),$$

with $U_a' = NQ' = U_a - \frac{1}{2}V$, $U_b' = SR' = U_b + \frac{1}{2}V$, $U' = U_{ab}$. For sufficiently large values of $\beta\delta$, with which we are here concerned, the above expression reduces approximately to

$$D = \exp\left[-\left\{(U_a - W_x - \tfrac{1}{2}V)/kT_1\right\}^{1/2}\right] \tag{24}$$

with the previous definition of T_1. In substituting this into (23) we must put $W_x = W_a$. We thus get the same expression for D as in the case of two identical metals, with the only difference that the "work function" $U_a - W_a$ is replaced by

$$U_a - W_a - \tfrac{1}{2}V = \tfrac{1}{2}[(U_a - W_a) + (U_b - W_b)] \tag{25}$$

that is by the arithmetric mean of the work functions of the two metals.

Now if V is increased by $V_1 \ll V$ the transmission coefficient is changed by the amount $(\partial D/\partial V)V_1$ where

$$\frac{\partial D}{\partial V} = \frac{D}{4[\frac{1}{2}kT_1(U_a - W_a + U_b - W_b)]^{1/2}}$$

Introducing this expression and the expression (24) in (11) and putting for the sake of brevity

$$[2kT_1(U_a - W_a + U_b - W_b)]^{1/2} = \theta \tag{26}$$

we have

$$\alpha_2 = \frac{2\pi}{m^2}\frac{1}{2\theta}\int_0^\infty dW D(W)\{f_b(W + U') + \theta f_b'(W + U')\}$$

or so long as θ is small compared with $W+U'$

$$\alpha_2 = \frac{\pi}{m^2\theta}\int_0^\infty dW D(W) f_b(W + U' + \theta). \tag{27}$$

Comparing this (8) we see that

$$\alpha_2 = \alpha_1'/2\theta \tag{28}$$

where α_1' is the value taken by the coefficient α_1, if U is increased by θ. It may be remarked that α_1, is connected with the "specific conductivity" of the gap σ_g by the relation

$$\sigma_g = e^2\delta\alpha_1.$$

Now α_1', is but slightly different from α_1, since θ is assumed to be small, so that we can finally put $\alpha_2 \leqq \alpha_1/2\theta$. This relation could be of course obtained directly by neglecting the first term in the integral (11) which does not take account of the change of the transmission coefficient D caused by the introduction of the additional potential difference V_1. It can be easily shown that the ratio of this term to the second term, which just characterized this change, is approximately equal to

$$\frac{\theta}{U_a - W_a + U_b - W_b} = \left(\frac{2kT_1}{U_a - W_a + U_b - W_b}\right)^{1/2}$$

that is, remains very small for values of T_1 corresponding to gaps of the width $\delta = 10A$ or even less than that.

The "characteristic curve" of our contact, considered as a rectifier, is thus the parabola

$$I = \alpha_1 V_1(1 + V_1/2\theta)$$

This equation holds, of course, for sufficiently small values of V_1 only. It follows from it that the rectifying action of the contact becomes prominent for values of $|V_1|$ which are of the same order of magnitude as θ. Using the previous value of $T_1 = 120°$ which corresponds to 0.01 volts and assuming for the mean work function of the two metals $\frac{1}{2}(U_a - W_a + U_b - W_b)$ a value corresponding to 4 volts, we get for θ about 0.4 volts.

This is a rather large figure, which explains the fact that metallic contacts cannot be used as detectors for radio-oscillations of small amplitude.

It seems possible, however, on our scheme to explain the detector action of contacts between metals and some semi-conducting "crystals" used for this purpose in simple radio receivers, by assuming that in these bodies we have to deal with a distribution of electrons different from that of Fermi.

The simplest assumption would be to replace the Fermi distribution by the usual Maxwellian one, corresponding to a relatively small number of free electrons per unit volume. This can be considered as a particular case of the preceding theory, since the Maxwell distribution is the limiting case

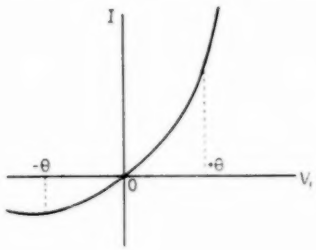

Fig. 4.

of the Fermi distribution which may be specified by putting the maximum kinetic energy of the electrons at $T=0$ equal to zero. It is clear that in this case the semi-conductor will play the role of the body a and the metal that of the body b, so that we shall have $W_a=0$, $V=U_a-(U_b-W_b)$, etc.[11]

It seems at first sight that this will leave our formulas for α_1, and α_2 unaltered since they depend upon the distribution function of the body b only and not on that of the body a. That this is not so, is clear, however, from equation (23), which with $W_a=0$ and $v_a=0$ would give $\sigma_g=\infty$. This shows that some of the approximations used in the evaluation of α_1, and α_2 no longer hold in the limiting case we are now considering.

We shall not try to adjust our calculations to this case, for the implied picture of a semi-conductor as of a box enclosing a rarefied electron gas seems hardly adequate enough to deserve a quantitative treatment. It is, however, directly apparent without any calculations whatsoever, that the rectifying effect of a contact between two bodies, so far as it depends upon their dissimilarity with respect to the concentration and the velocities of the electrons, must increase for a given absolute value of V_1 as this dissimilarity becomes more pronounced.

A satisfactory extension of the above theory to the case of contacts between a metal and a semi-conductor, or between two semi-conductors will be possible only after an at least crude electron theory of such semi-conduc-

[11] We have designated with a that body for which the potential energy (inside) is higher than for the other when equilibrium is reached, that is, when the straight lines representing the kinetic energies W_a and W_b lie on the same level (that is, coalesce with each other).

tors shall have been developed. It will be further necessary to take account of the fact that in actual contacts the distance δ between contiguous surfaces does not remain constant, but varies in a more or less periodic manner, within a certain range, and that the adjacent (curved) surfaces of the two bodies need not be equipotential surfaces, as is the case if they are far apart.

X-RAY ABSORPTION IN GASES

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Abstract

X-ray spectral lines reflected from a platinum surfaced mirror and by a calcite crystal have been used for absorption measurements with neon, sulphur dioxide, chlorine and argon. The double reflection gives a more nearly homogeneous beam, since the mirror greatly reduces the higher orders of the shorter wave-lengths. The results are summarized in the following table.

Mass Absorption Coefficients

	0.496A	0.561A	0.631A	0.710A	1.389A	1.539A	2.288A
Ne	0.84	1.20	1.69	2.50	16.0	23.4	75.5
Al	1.96	2.71	3.82	5.32	37.3	50.7	149.6
SO_2	1.92	2.67	3.60	5.55	38.5	51.8	162.6
S (Calc)	3.40	4.64	6.89	9.96	66.4	88.4	284.0
Cl	4.14	5.76	8.18	11.52	76.9	102.7	315.0
A	5.06	6.89	9.80	13.0	85.7	114.0	339.4

Introduction

AN EXAMINATION of the tabulated values of x-ray absorption coefficients[1] reveals the scarcity of data for gases. In spite of the chances for contamination, gases are to be preferred to solids in some cases of absorption measurement. With the longer wave-lengths in particular, the thickness of solid absorbers is so small that the question of homogeneity presents serious difficulties. Such is not the case with gases.

In the present work neon, sulphur dioxide, chlorine and argon were studied. For comparison purposes, readings were also taken with aluminum. The K_α and K_β lines of silver, molybdenum and copper and the K_α line of chromium were used with each material.

Apparatus

In order to secure significant absorption data, especial precautions were taken to obtain homogeneous x-rays of known wave-length, as well as to insure the purity of the absorbing materials. Homogeneity was obtained by totally reflecting the x-rays from a platinized mirror, and then selecting a strong spectral line by diffraction from a calcite crystal. The angle of the mirror can be so adjusted that the desired wave-length λ is totally reflected, whereas for wave-lengths $\lambda/2$, $\lambda/3$, etc. the glancing angle of incidence is greater than the critical angle and no appreciable reflection occurs. It is thus possible to apply relatively high potentials to the x-ray tube without danger

[1] International Critical Tables, Vol. VI, p. 12.

of introducing higher order reflections, an especially valuable feature for the longer wave-lengths.

The arrangement of the apparatus is shown in Fig. 1. The x-rays, after reflection from the platinized mirror *b*, traversed the absorption cell *c*, and were then reflected from the calcite crystal *d* into the ionization chamber. The figure is drawn approximately to scale.

For the source of x-rays, water cooled tubes of the Coolidge type were used. The Mo target tube was supplied by the Victor X-Ray Corporation; the silver, copper and chromium tubes were made by Siemens Reiniger Veifa. Lindemann glass windows in the latter two tubes avoided great absorption in the walls. As a source of high voltage a high tension transformer without

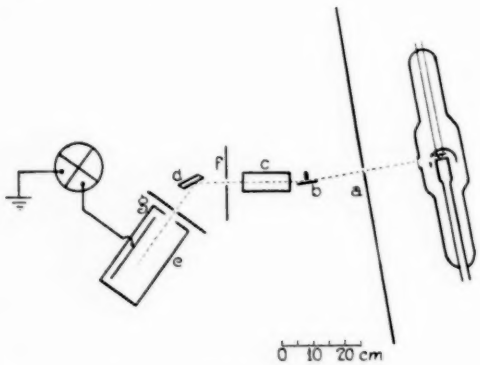

Fig. 1. Diagram of apparatus.

rectification was found satisfactory. An auto transformer and rheostat in the primary circuit served to control the voltage. The primary of the filament transformer was connected, through a variable resistance, across the primary of the high tension transformer. In spite of this precaution, however, it was not possible to eliminate completely the effect of fluctuations of the line voltage.

The spectrometer was of the double crystal type, designed by A. H. Compton, and constructed by the Societe Genevoise. The platinized mirror was placed in the position of the first crystal. A Compton electrometer was used for current measurements. The insulation was sulphur, and the ionization chamber was filled with argon.

The Absorption Cells

Since one of the chief problems in working with gases is the obtaining of pure samples and the maintaining of that state during the observations, particular care was used in the selection of containers for the gases. Three types were used during the experiment. Fig. 2a represents the first type. These cells were made by fusing very thin glass windows to Pyrex tubing of the size indicated. Being curved, the windows could be made quite thin and yet stand atmospheric pressure during outgassing. This cell has the advantage that it may be thoroughly outgassed and that there is very little

chance of contamination after a cell is once filled and sealed off. The second type, Fig. 2b, was obtained by closing the ends of the Pyrex tubing with brass pieces which had narrow rectangular openings in the ends. These openings were covered with thin celluloid windows which were attached to the brass by means of "Duco Household Cement." The brass to glass connection was made by means of wax. The third type, Fig. 2c, was quite similar to the second. In this case, however, plane glass windows were fused to the tubing, rectangular slits cut in these windows and celluloid cemented over these openings. The third type was used only as a check on the second to see if any appreciable contamination might be detected by such a comparison.

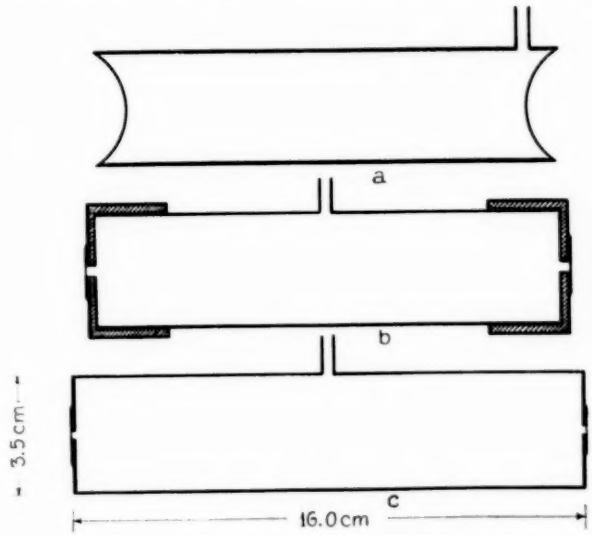

Fig. 2. Diagram of three types of cell used.

A cell of type *a* could be attached directly to the vacuum line, outgassed by baking for several hours, and filled with a purified gas without having the gas come in contact with anything except glass. For this reason seven such cells were used The other cells were preferable however when the absorption in the glass windows became so great as to prevent accurate observations.

Purification of chlorine and sulphur dioxide was by a partial distillation method. The gas as furnished commercially was dried and solidified by cooling. Any unsolidified matter was removed by the vacuum system. On raising the temperature of the solidified material a few degrees above the boiling point of the particular gas the entire system was filled with the gas. The cell was then sealed off at an observed temperature and pressure. The neon was furnished in flasks, specially purified, by the Air Reduction Company. One cell was filled with argon furnished by the Air Reduction Company as pure. A second was filled with argon purified by means of a misch metal arc. A third cell was filled with argon containing known percents of impurities. As these three gave, on correction of the third, very nearly the same results,

gas of the last mentioned type was used throughout the latter part of the experiment.

The Data

A test of the homogeneity of the beam was made by means of Al foil. Three or more samples of aluminum were used in every case, and they were so selected as to give a total absorption of the same order of magnitude as with the gas-filled cells. If the values of the mass absorption coefficients with the various samples showed no decrease greater than the experimental error, it was assumed that the beam was sufficiently nearly homogeneous for the purposes of the experiment.

In order that the absorption of the gas be separable from that of the cell, readings were taken in each case with the cell evacuated and then filled to a measured pressure. Since, in several cases, the absorption by the gas was only a small part of the total measured quantity, it was very important that the cells be placed in the same position for all readings. Precautions were taken to insure that this be the case.

Corrections for the impurities in the argon were obtained by calculation from the Eq. (1)

$$m(\mu/\rho) = m_1(\mu/\rho)_1 + m_2(\mu/\rho)_2 + \text{etc.} \qquad (1)$$

m being the mass and μ/ρ the mass absorption coefficient of the mixture; the terms on the other side of the equation representing the same quantities for the constituents. For the longer wave-lengths, values of μ/ρ for nitrogen and oxygen were obtained from table values by extrapolation. The data for sulphur were obtained from the sulphur dioxide values of the atomic absorption coefficients by subtracting the oxygen values in a similar manner.

In every case, the times for the rates of deflection over the same range were taken with the absorber alternately in and out of the path of the x-ray beam. These times were corrected for natural leak. From twenty-five to two hundred such pairs of readings constitute a single "set."

Data for four gases using a single cell and a single wave-length, K_α of Mo, are shown in Table I. Here i_1/i_0 represents the ratio of the transmitted to the incident intensity, μ/ρ is the mass absorption coefficient and μ_a the atomic absorption coefficient. The argon used in cell 5 contained 3% nitrogen and 0.4% oxygen. Corrected value = 85.6. The value of S from the SO_2 value = (58.13 − 5.28) = 52.8.

Table I. *Kα of Mo.* ($\lambda = 0.710$).

Cell	Absorber	Density (g/cc)	i_1/i_0 (Evac.)	i_1/i_0 (Filled)	μ/ρ	$\mu_a \cdot 10^{23}$
5	Ne	0.000512	0.6093 ± 1/7%	0.6000 ± 1/7%	2.42	8.07
5	SO_2	.002045	.6093	.5280	5.50	58.13
5	Cl	.00166	.6093	.4780	11.44	66.92
5	A	.001589	.6093	.4700	12.78	84.1

In a similar way data were obtained for the other wave-lengths and using various absorption cells, giving the results summarized in Table II.

TABLE II. *Mass absorption coefficients.**

Substance	AgK_β .496A	AgK_α .561A	MoK_β .631A	Mo$K\alpha$ .710A	CuK_β 1.389A	CuK_α 1.539A	CrK_α 2.288A
10 Ne	.84	1.20	1.69	2.50	16.0	23.3	75.5
13 Al	1.96	2.71	3.82	5.32	37.3	50.7	149.6
SO_2	1.92	2.67	3.60	5.55	38.5	51.8	162.6
16 S (Calc)	3.40	4.64	6.89	9.96	66.4	88.4	284.0
17 Cl	4.14	5.76	8.18	11.52	76.9	102.7	315.0
18 A	5.06	6.89	9.80	12.98	85.7	114.0	339.4

	Atomic absorption coefficients $\times 10^{23}$						
Substance	0.496A	0.561A	0.631A	0.710A	1.389A	1.539A	2.288A
10 Ne	2.8	4.0	5.63	8.33	53.3	77.6	252
13 Al	8.76	12.1	17.1	23.8	167	226	668
16 S	17.9	24.4	36.3	52.5	350	466	1497
17 Cl	24.2	33.7	47.8	67.4	450	601	1843
18 A	33.3	45.3	64.5	85.4	564	750	2233

Fig. 3 shows curves obtained by plotting $\log_e \lambda$ and $\log_e \mu/\rho$. Empirical

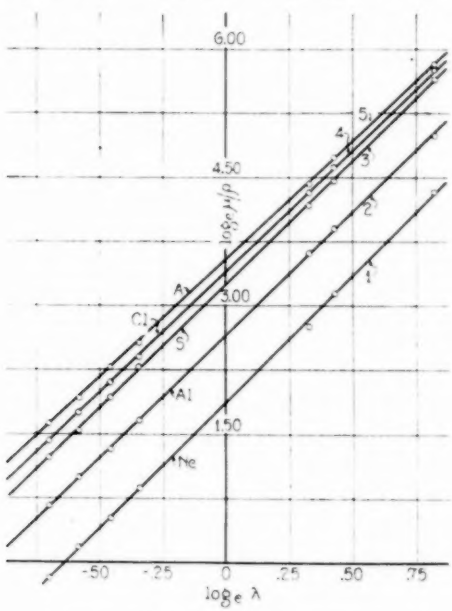

Fig. 3. Plot of $\log_e \lambda$ and $\log_e \mu/\rho$.

equations which represent these lines are as follows:

$$\text{(Ne)} \quad \log_e \mu/\rho = 2.92 \log_e \lambda + 1.87, \text{ or } \mu/\rho = 6.5\ \lambda^{2.92} \tag{2}$$

$$\text{(Al)} \quad \log_e \mu/\rho = 2.88 \log_e \lambda + 2.67, \text{ or } \mu/\rho = 14.45\lambda^{2.88} \tag{3}$$

$$\text{(S)} \quad \log_e \mu/\rho = 2.90 \log_e \lambda + 3.25, \text{ or } \mu/\rho = 25.8\ \lambda^{2.90} \tag{4}$$

$$\text{(Cl)} \quad \log_e \mu/\rho = 2.84 \log_e \lambda + 3.40, \text{ or } \mu/\rho = 30.0\ \lambda^{2.84} \tag{5}$$

$$\text{(A)} \quad \log_e \mu/\rho = 2.77 \log_e \lambda + 3.45, \text{ or } \mu/\rho = 34.5\ \lambda^{2.77}. \tag{6}$$

* An analysis of a sample of the aluminum used showed 0.45 percent iron. The values of the mass absorption coefficient for Al given in Table II are therefore too high for pure Al.

A comparison of experimental values with values calculated from these equations shows, in the majority of cases, discrepancies less than one per-cent.

Discussion of Results

From the equation

$$I_1 = I_0 e^{-\mu x} \tag{7}$$

it follows that

$$\mu/\rho = (-\log_e I_1/I_0)/\rho x \tag{8}$$

where I_1/I_0 is the ratio of the transmitted intensity to the incident intensity, μ is the linear absorption coefficient, x the thickness and ρ the density of the absorber. In order that the value I_1/I_0 be for the gas only it is necessary to use the ratio i_1/i_0 (filled) to i_1/i_0 (evacuated), i.e., for this calculation, $I_1/I_0 = (i_1/i_0)f/(i_1/i_0)_{ev}$. The uncertainty in the value of μ/ρ is therefore increased. The length x was known to about 1/3 percent, the value of the density to 1/5 percent and the value of i_1/i_0 to 1/7 percent. The value of I_1/I_0 is however by no means so accurate. A comparison of the data of Tables I and II shows that for neon in particular the uncertainty is rather large. This obviously results from the fact that the absorption by the gas was so small a part of the total measured quantity. In the case of gases of larger atomic number and even for neon at the longer wave-lengths this uncertainty is greatly diminished.

Other data for these gases, with which to compare the present results, are very meagre. Wingardth[2] has obtained some measurements on chlorine gas for $\lambda = 0.586$, 0.631 and 0.709A. For the latter wave-length he finds $\mu/\rho = 11.9$, which compares acceptably with the value 11.52 here obtained. Barkla and Collier[3] also made some measurements many years ago on the absorption of fluorescent x-rays in sulphur dioxide. Because of the lack of true homogeneity, their data are of little significance for a precise comparison, though the agreement with the present results is as good as can be expected. Because of this lack of other existing absorption data, for these substances, the present data are perhaps of especial value.

In conclusion, I wish to express my appreciation to Professor A. H. Compton for his suggestions and interest both preceding and during the period of experimental work.

[2] Wingardth, Dissertation, Lund, 1923.

[3] Barkla and Collier, Phil. Mag. **23**, 987 (1912).

DIFFRACTION OF X-RAYS IN LIQUIDS: EFFECT OF TEMPERATURE

By E. W. Skinner
University of Iowa

(Received October 15, 1930)

Abstract

The effect of temperature upon x-ray diffraction has been examined for the following liquids: mesitylene, 4-hydroxy-1.3-dimethylbenzene, 2-hydroxy-1.3-dimethylbenzene, phenol, napthalene, benzene, cyclohexane, di-n-propyl carbinol, heptylic acid, tertiary butyl alcohol, lauryl alcohol, octane, 2.7-dimethyloctane and 2.4-trimethylpentane. (1) The peaks shift in the intensity-diffraction angle curve toward smaller angles with increase in temperature, which varies in amount in different planar spacings in the same liquid; (2), the peak intensity varies with temperature differently for the different spacings in a single liquid, the principal maxima showing a decrease in the intensity for some liquids (class I), and an increase in the intensity for other liquids (class II) with increase in temperature; (3) a greater diffuseness of the principal maxima was found at high temperatures, attaining a greater magnitude for class I liquids; (4) the percentage increase in peak width per degree change in temperature is greater for class II than for class I; (5) boiling had no effect on diffraction phenomena, (6), increased scattering at small angles was noted at high temperatures, the effect being greater for class II.

The foregoing results lead to the following conclusions. The evidence favors strongly the cybotactic space group condition of liquids and indicates that in some of the liquids space rearrangement within these groups takes place with changes in temperature. It may be said there is a change in molecular shape. Furthermore, within the groups of some liquids, expansion is apparently different in different directions, or internally anisotropic.

RESEARCHES carried on in this laboratory and elsewhere[1] on the diffraction of x-rays in liquids indicate that the molecular arrangement in a liquid consists of fairly orderly though temporary groups produced by molecular forces. These forces are most effective in producing such a regularity in unsymmetrical molecules. The groups evidently have neither perfect form nor sharp boundaries. Although numerous incidental suggestions as to the somewhat crystalline arrangement of molecules in a liquid antedate the work of this laboratory, yet it has been here that such a description, termed the "cybotactic condition," has been actively adopted and attempts have been made to establish its certainty by every systematic means of approach. Thus, the effect of increase in length of chain, and the differences in molecular arrangement of alcohol molecules with point of attachment of OH have been discovered. A determination of the influence of temperature is clearly of importance in such a study.

[1] See papers by Stewart and co-workers in Phys. Rev. 1927–1930; Stewart, Rev. Mod. Phys. **2,** 116 (1930); Stewart, Chem. Rev. **6,** 483 (1929); Drucker, Phys. Zeits. **29,** 273 (1928).

Apparatus and Method

The x-ray spectrometer used, and the method of procuring diffraction curves were essentially the same as described by Stewart and Morrow.[2] The furnace for heating the liquid consisted of two coils of nichrome wire wound about two pieces of one inch iron pipe, each 2.5 inches long. The wire was insulated from the iron with asbestos. The heating coils were mounted vertically, one above the other, leaving room between their near ends for the passage of x-rays. The liquid was contained in a thin walled glass tube and placed so as to intercept the primary beam in this space. The thin walled

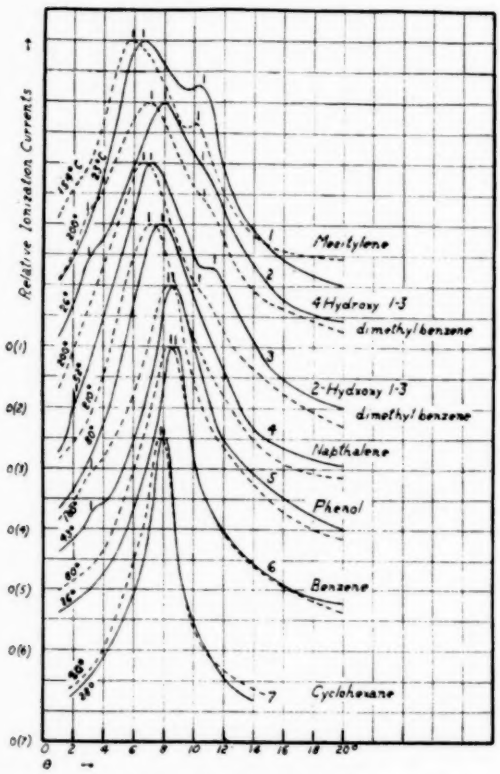

Fig. 1. Relative intensity liquid diffraction curves at two different temperatures.

glass tube was fused to a heavier tube leading to a Graham reflux condenser. The temperature was measured by means of a calibrated constantan-copper thermocouple, enclosed in a thin-walled capillary tube and inserted in the liquid.

The diameter of the tube containing the liquid was made definitely less than the optimum thickness of each particular liquid under observation, in order that there might be no effect from general radiation. The diffraction peaks obtained are produced by the Mo $K\alpha$ radiation. The voltage on the tube was such as to cause the maximum of the general radiation to fall at

[2] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

about 6°. The curve for cyclohexane in Fig. 1 indicates the absence of any important effect of general radiation.

RESULTS

The diffraction curves are given in Figs. 1 and 2, the dotted curves giving the data for the higher temperatures. Both sets are plotted to the same scale, hence, in Figs. 1 and 2 intensity comparison can be made only for a single curve. In Table I, the values for percentage change in intensity were obtained from the original data, before reduction as shown in Figs. 1 and 2. The following facts are drawn from these curves and Table I.

TABLE I. *Effect of change in temperature on the planar dimensions.*

Liquid	Temperature	d_1 (A.U.)	d_2 (A.U.)	d_3 (A.U.)	Percentage change in intensity of peak corresponding to d_1, d_2, d_3, respectively.
1. Mesitylene	23°C	—	6.00	3.86	—
Mesitylene	154°C	—	6.92	3.96	+18.0, −42.3
2. 4-Hydroxy 1.3 dimethyl benzene	26°C	14.0	5.10	3.86	—
	200°C	13.6	5.75	3.82	+80.0, +5.1, −30.0
3. 2-Hydroxy 1.4 dimethyl benzene	52°C	17.1	5.76	3.79	—
	200°C	—	6.17	3.92	+12.7, −37.8
4. Naphthalene	80°C	—	5.17	—	—
Naphthalene	210°C	—	5.76	—	+4.7
5. Phenol	43°C	12.7	4.73	—	—
Phenol	180°C	12.7	4.92	—	−38.0, +2.8
6. Benzene	26°C	—	4.64	—	—
Benzene	80°C	—	4.80	—	−1.1
7. Cyclohexane	28°C	—	5.08	—	—
Cyclohexane	80°C	—	5.24	—	−14.0
8. Di-n-Propyl Carbinol	24°C	10.2	4.87	4.35	—
Di-n-Propyl Carbinol	153°C	10.2	4.87	—	−6.7, +18.9
9. Heptylic Acid	28°C	17.7	4.64	—	—
Heptylic Acid	193°C	18.5	4.80	—	+18.5, −12.2
10. Tertiary Butyl Alcohol	27°C	8.51	4.80	—	—
Tertiary Butyl Alcohol	80°C	8.88	4.90	—	−37.7, +9.8
11. Lauryl Alcohol	27°C	22.7	4.54	—	—
Lauryl Alcohol	140°C	24.0	4.80	—	−2.4, −5.6
12. Octane	27°C	—	4.54	—	—
Octane	120°C	—	4.70	—	−7.3
13. 2.7-Dimethyloctane	27°C	—	4.75	—	—
2.7-Dimethyloctane	150°C	—	5.17	—	−10.3
14. 2.2.4 Trimethylpentane	27°C	—	5.67	—	—
2.2.4 Trimethylpentane	92°C	—	5.91	—	+0.5

Explanation: d_1 represents the planar distance given by the small maximum on the small angle side of the principal maximum; d_2 the distance given by the principal maximum; and d_3 the third dimension given by the remaining maximum when present.

(1) In general the maxima shifted toward the smaller angles of scattering with increase in temperature, the principal maxima being most consistent in this regard. The small peaks, denoting the largest spacing, showed no change in dimension except for tertiary butyl alcohol(10).

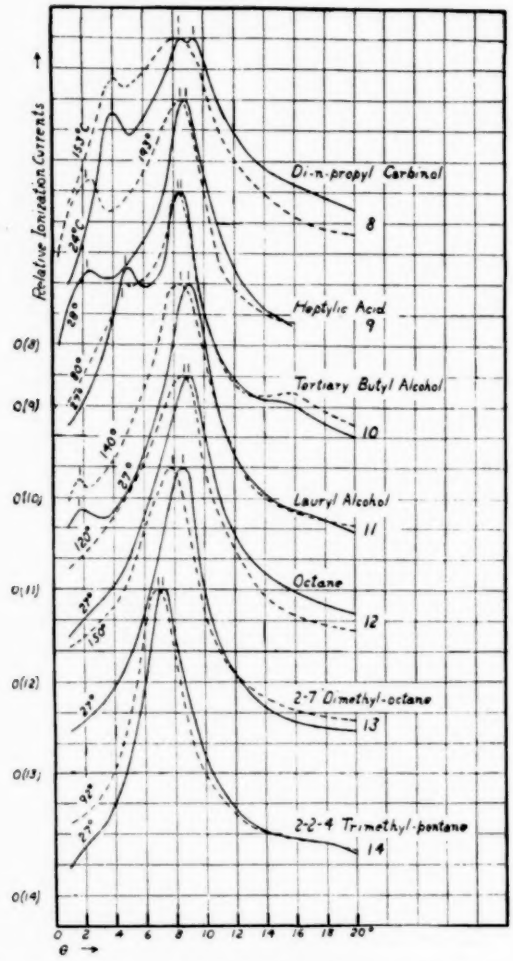

Fig. 2. Relative intensity liquid diffraction curves at two different temperatures.

(2) The effect of temperature upon the intensity is not uniform for all the liquids. In this respect, the liquids fall under two classifications:

Class I. Those liquids whose principal maxima show a decrease in intensity with increase in temperature, including nos. (6), (7), (9), (11), (12), and (13). (See Table I).

Class II. Those liquids whose principal maxima show an increase in intensity with increase in temperature, including nos. (1), (2), (3), (4), (5), (8), (10), and (14).

In general the smaller maxima in all liquids showed a decrease in intensity with increase in temperature.

(3) An increase in general scattering at small angles with increase in temperature was found in all cases, the increase being greater for liquids of class II.

(4) No observable difference in peak intensity was noted between that at the boiling point of tertiary butyl alcohol and a temperature a few degrees less.

(5) The percentage increase in peak width per degree change in temperature is five times as great for the liquids of class I, as for class II. As a matter of fact a graph showing the percentage change in peak width with difference in temperature is linear for both classes.

(6) A second order peak was noted in the case of tertiary butyl alcohol, but owing to the extreme diffuseness no conclusions regarding intensity change can be drawn.

These results may be compared with those obtained by Vaidyanathan[3] who studied the influence of temperature on the haloes of camphene, mesitylene, acetic acid, butyric acid and ethyl alcohol, varying the temperature from 30° to 120° and 150°C. He observed a contraction of the haloes, an increase in their diffuseness and an increase in the scattering at small angles in all cases. In the case of liquids with two haloes, with rise of temperature, the separation between the inner and the outer halo tends to be effaced and the inner haloes become diffuse more quickly than the outer ones. As will be observed the results herein presented are in general agreement with those just cited, but not in detail.

Discussion and Possible Interpretation of Results

(1) In general the effect of temperature upon liquid scattering is similar to the same effect in powdered crystals. This favors the conception of groups possessing space arrangement, simulating the effects of powdered crystals.

(2) The most obvious cause for the increase in planar dimension with increase in temperature is thermal expansion. A comparison of the expansion coefficients for d_2, for example, as computed from the x-ray data, with corresponding values given in the International Critical Tables, shows no agreement. In fact, in some cases it showed as high as three times the true value. Furthermore, the expansion in molecular spacing in different directions in one liquid group is not the same. In consideration of these two facts, one is led to advance a new view of expansion in liquids which admits the possibility of anisotropic expansion within each group. Such a condition is common in crystals. The actual mechanism of expansion in the liquid might include an increase in warping of the molecules with increasing temperature. Such a warping might alone cause a decrease in separation of molecules in one direction and an increase in a direction perpendicular thereto. Such a condition of unequal expansion comparable to that of a crystal is not possible unless there exists, as is claimed, a temporary regularity of molecular arrangement in groups. This is designated as the cybotactic condition.

[3] Vaidyanathan, Ind. Jl. Physics, III, III, 391, (1929).

(3) In the case of the liquids of class II, there is evidence of a group rearrangement, or a change in molecular shape causing such rearrangement. shown in (a) the increase in coherent scattering with increase in temperature. and (b), the small percentage increase in peak width per degree increase in temperature in comparison with class I liquids. This evidence, and that in the preceding paragraphs are not sufficient to assert that the rearrangement of groups actually occurs, but this interesting hypothesis seems a reasonable and straightforward explanation for the action of some liquids.

(4) In the case of the liquids in class I, the intensity decreases with an increase in temperature, and may be accounted for by two factors: (a) the decrease in density of the liquid due to the thermal expansion, (b) the disturbance of group regularity due to increased thermal agitation. That the first cause is not the only one, was proved by a special experiment. The relation between the intensity of the principal maximum and the mass intercepted by the primary beam was determined experimentally for cyclohexane. The actual change in mass intercepted over the given temperature change was computed, and the loss in intensity due to expansion determined. This was found to be 4 percent, whereas the actual loss was 14 percent.

In the view of the workers in this laboratory, the cybotactic condition is one in which at any instant small regions, occurring frequently throughout the liquid, have effective regularity of molecular spacing. A moment later a similar description applies, but with the regions of regularity altered in positions. Between these regions are to be expected less regularity of arrangement. But there are no sharp boundaries of regions of regularity of structure. Neither is there entire randomicity anywhere. But with any failure to comply with perfect crystalline form, there would be a lack of coherent scattering and hence greater diffraction near the zero angle of diffraction. Class II, in which the group structure seems to be altered with increase in temperature, also shows a greater increase with temperature of the scattering near the zero angle than do the liquids of class I. These two phenomena are definitely correlated in the liquids here used. As could be anticipated from the view here stated, an increase in scattering near zero angle of diffraction would be caused by increase in temperature for all liquids. This expectation is verified.

The boiling point, in the very nature of the case, has no relation to the group arrangement of molecules. As should be expected, the approach to boiling point produced no marked alterations in the diffraction curves. As will be observed all of the results of these experiments are in accord with the conception that in the liquid state, the cybotactic condition is generally found.

The author wishes to take this opportunity to express his appreciation of the cooperation of the staff of the Physics Department and his thanks to Professor G. W. Stewart for his suggestions and inspiration in carrying on this research.

ON THE FLUORESCENCE OF QUARTZ UNDER THE INFLUENCE OF CATHODE RAYS OF LOW VOLTAGE

By Heinrich Peters, Rheydt
(Based upon experiments made in collaboration with Th. Schultes, Darmstadt)

(Received September 17, 1930)

Abstract

Some experiments on the production of a red fluorescence in glass and quartz by cathode rays are described. It was found that the red glow could be produced in highly evacuated tubes and that the presence of oxygen or other gases was not essential. This is contrary to the conclusion of Wood. A spectroscopic study of the fluorescence showed a continuous spectrum with two maxima in the red, one in the green and one in the blue. No trace of any oxygen line was found. The observation that the red fluorescence disappears after about 70 hours of bombardment indicates that the SiO_2 group in the glass goes over into an allotropic modification.

LILIENFELD[1] found that, under certain conditions, the discharge of electricity through rarefied gases was accompanied by a red (instead of the usual green) fluorescence. The red fluorescence appeared in tubes which had been flushed with oxygen and then evacuated to a pressure less than 0.01 mm Hg. Lilienfeld regarded the phenomenon as due to the bombardment by slow cathode rays of the glass walls on which a gas (probably oxygen)was occluded.

E. Goldstein[2] reported that he also noted the red fluorescence not only of glass but of other substances, such as rock crystal, fused quartz, etc., which contain SiO_2. Since the fluorescence appeared not at all in tubes containing N_2, H_2, CH_4, He or A, weakly with air and strongly with oxygen, he concluded also that oxygen was an essential factor in the production of the fluorescence.

On the other hand Konen[3] pointed out that he could obtain the red fluorescence in tubes filled with helium. He suggested that CaO, present in minimal amounts, might constitute the fluorescent centers but admitted the difficulty of discriminating between this hypothesis and that of Lilienfeld and Goldstein.

Gehrke and Reichenheim[4] examined the red fluorescence spectroscopically and found a continuous spectrum between 654–620 mμ with two maxima in intensity at 650 and 630 mμ. Superposed on this was a continuous spectrum of all colors with a broad maximum in the blue.

Quite recently Wood[5] has found the same red fluorescence accompanying the excitation of gases at very low pressures by high-frequency ($\lambda = 4$m), low-potential discharges. According to Wood the red glow appears only in

[1] I. E. Lilienfeld, Ber. d. deutsch. Phys. Ges. p. 631 (1906); Ann. d. Physik **32,** 673 (1910).
[2] E. Goldstein, Ber. d. deutsch. Phys. Ges. p. 598 (1907).
[3] E. Konen, Ber. d. deutsch. Phys. Ges. p. 774 (1907).
[4] Gehrke and Reichenheim, Ber. d. deutsch. Phys. Ges. p. 593 (1907).
[5] R. W. Wood, Phys. Rev. **35,** 673 (1930).

very well cleansed tubes and goes over into a green fluorescence when the potential is increased. In this case a red fluorescent spot appears on the wall opposite the green fluorescence.

According to Wood the red fluorescence does not appear promptly after application of the potential but appears gradually in a few seconds or minutes, and is sometimes preceded by a green fluorescence. Further he remarks that if a bright discharge is produced at one end of the tube with a single ring electrode until the glass fluoresces with a red color and the ring is then moved to the other end, there will be no red fluorescence there. He concludes that some chemical alteration of the glass must be essential to the fluorescence. The red fluorescence could not be excited by the field of a 30m oscillator but after it had appeared in the field of a 2m oscillator it could be maintained by the 30m oscillations. Stroboscopic investigations showed that the excitation was by electron rays having a definite direction and that there was no special property of the high frequency discharge involved.

Spectroscopic examination established that, in addition to the continuous spectrum in the red, lines of the oxygen spectrum always appeared. For this reason Wood believed that the presence of oxygen was a necessary factor in the red fluorescence.

Independently, the author[6] has also observed the red fluorescence under experimental conditions similar to those of Wood.[5] Since the experimental results differ in some respects from those of Wood, it would seem appropriate briefly to mention them here.

Tubes of widely varying length were used. The electrodes were external and were excited by a vacuum tube oscillator. The oscillator in some of the experiments was of the push-pull type described by Eccles and Jordan.[7] The wave-length was 6–7 meters and the output 150 watts. The potential was transmitted to the experimental tube by placing it at the loop position in an inductively coupled Lecher system (Figs. 1–3).

By varying length and diameter of the tubes it was found that the fluorescence was strongest in short, narrow tubes, i.e., in those in which the current density was greatest. In the wide tubes the glow did not appear unless the cathode rays were concentrated on individual spots by means of a magnetic field.

In other experiments a long-wave oscillator ($\lambda = 700$m) was used to determine whether or not a change of frequency materially affected the phenomenon. For these experiments a Hartley oscillator of about 80 watts capacity was used (Fig. 4). Oscillator and tube were connected by a Oudin resonator coil. In contrast to Wood's results it was found that all tubes showed the red fluorescence when excited by the long waves and that a preliminary excitation by short waves was not necessary. I believe that the difference which Wood observed between the long and short wave excitation was due to a difference in some discharge characteristic (probably potential) other than frequency.

[6] Peters and Schultes, Zeits. f. Elektrochemie, im Erscheinen begriffen.

[7] Eccles and Jordan, Electrician **83**, 299 (1919).

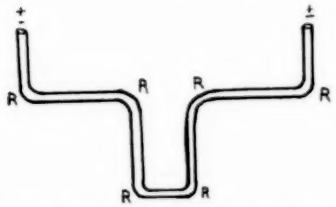

Fig. 1. Experimental tube of Lilienfeld for observation of the red phosphorescence at discharges with A.C. The points marked with *R* showed the red phosphorescence.

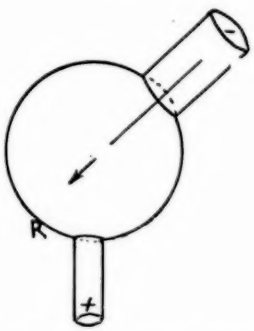

Fig. 2. Experimental tube of Lilienfeld for observations of the red phosphorescence at discharges with D.C. The point marked with *R* showed the phenomenon.

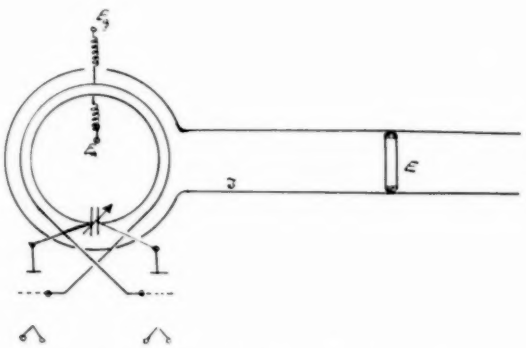

Fig. 3. Push-pull oscillator with inductively coupled Lecher system (*J*). *E* represents the experimental tube with exterior electrodes.

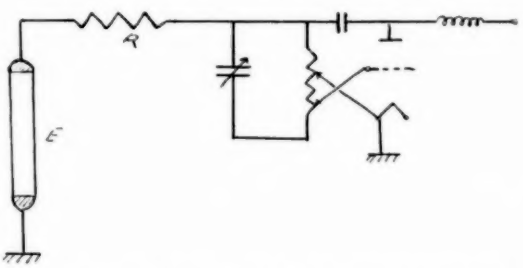

Fig. 4. Hartley oscillator, to which the experimental tube *E* is coupled by a resonator coil *R* of Oudin.

Experiments with internal electrodes also gave the red fluorescence at both high and low frequency alternating currents and with direct current.

When the high frequency current was led to the tubes through a suitable rectifier no new phenomena whatsoever appeared. It was observed that because of irregular field distribution the experimental tubes showed a detector action which makes the rise of cathode rays possible in one direction only. This observation corresponds with the stroboscopic experiments of Wood who found a periodic appearance of the fluorescence in rhythm with the alternating frequency. Experiments on the deflection of the cathode beam with a magnetic field showed that the red fluorescence was produced by electrons of lower velocity than those producing the green fluorescence. The "positive electron ray," thought by some authors to be the cause of the red fluorescence, appears to be a secondary electron ray moving in a direction contrary to the primary one.

Because the earlier spectroscopic observations[4] were made with tubes having internal electrodes it seemed worthwhile to repeat them with tubes having external electrodes which could as a consequence be more thoroughly cleaned. The tubes were raised to a high temperature (just under the melting point) and evacuated with a steel Gaede pump. The results of the spectroscopic study of the red fluorescence are as follows:

Beginning of the red fluorescence	723.8mμ
First maximum	642.5mμ
Minimum	633.8mμ
Second maximum	628.5mμ
End of the red phosphorescence	589.5mμ
Maximum in the green part	560.0mμ
Maximum in the blue part	479.0mμ

The spectrum of the fluorescence consists of a continuum in the red with two maxima close together and a broad continuum in the green and the blue. The values agree well with those of Gehrke and Reichenheim.[4]

In none of the nearly 100 spectral tests made, with exposure times up to more than 50 hours, *did an oxygen line appear.*

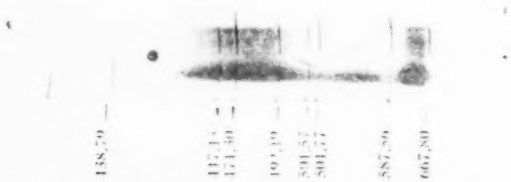

Fig. 5. Spectrographical test of the red phosphorescence. The lines are caused by a He-test, placed about in order to find the wave-length. The test shows that the red phosphorescence is a continuum and that no oxygen lines are present.

Fig. 5 gives a reproduction of one of the spectra. The double red as well as the green and blue maxima are to be seen distinctly. The lines visible in the figure are from helium and were added *subsequently* to serve as a wavelength guide. In order to make the two maxima in the red better visible, Fig. 6 shows a microphotometer curve of the spectrogram.

These spectroscopic results on heated, highly evacuated tubes proves that the red fluorescence will appear in the absence of any film of gas or water and that the presence of oxygen is not essential. This conclusion is at variance with that of Wood.

The red fluorescence was obtained with pure quartz also, which shows, in agreement with other publications,[2] that it is the SiO_2 group in the glass which is responsible for the fluorescence.

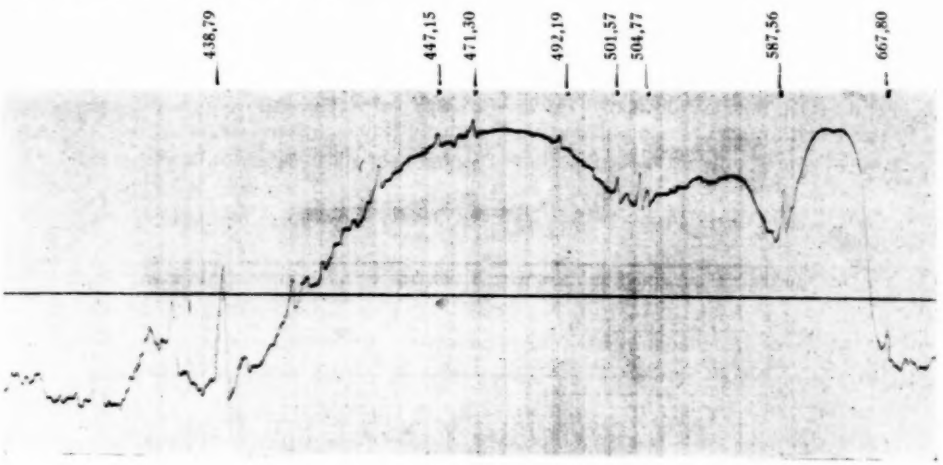

Fig. 6. Photometrical curve of the spectrographical test (Fig. 5). It shows distinctly the double maximum in the red part of the spectrum.

After continuously operating such tubes for nearly 70 hours it was found that the red fluorescence disappeared slowly. The points which had shown the red fluorescence now exhibited only the green fluorescence. Moreover, after having stood for weeks in an atmosphere of air, pure oxygen, hydrogen, steam, etc., the red glow did not appear again. The spectroscopic proof that the red glow is not due to oxygen is further strengthened by these results.

It has already been pointed out elsewhere[6] that these observations make it probable that under the influence of slow cathode rays the SiO_2 group changes to another modification. For the normal modification, stable under ordinary conditions, I propose the name "erythrokeretic." Under the influence of slow cathode rays during the red fluorescence it changes to an allotropic form for which the proposed name is "lacinokeretic." This latter form has less energy and it is not possible to reduce it under simple conditions (heating, etc.) into the erytherokeretic form.

The existence of these two modifications is shown only by spectroscopic analysis and would probably be very difficult to demonstrate by more direct means. The only known method for transforming from one to the other is by bombardment by slow cathode rays and here the change takes place in a layer of minimal thickness. Nevertheless the possibility exists that the phenomena of poisoned quartz catalysers may find their explanation in this allotropy.

PRESSURE AND HIGH VELOCITY VAPOUR JETS AT CATHODES OF A MERCURY VACUUM ARC

By E. Kobel
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(Received October 10, 1930)

Abstract

The amount of vaporization of copper from the cathode of a copper arc measured by Tanberg as well as the velocity of this vapour calculated from the force of reaction on the cathode, agree closely with the values obtained by another method from the cathode of a mercury arc. With a mercury arc and fixed cathode spot the mercury vaporization is 0.017×10^{-3} gr/amp. sec. and the vapour velocity 16 to 43×10^5 cm/sec.

Introduction

During attempts to fix the rapidly moving cathode spot of the mercury arc in a conical tungsten insertion-piece, it was observed that when the entire surface of the mercury was covered by the cathode spot the force exerted on the mercury was considerable. The following experimental tests were carried out during the first six months of 1929 with the object of measuring this force. In the meantime, Mr. Tanberg[1] had published a description of a quantitative investigation of the force exerted on the cathode of a copper arc, and although the methods of measurement and the cathode materials are very different, the results agree very closely.

Description of Experiments

Fig. 1 shows diagrammatically the 3-anode rectifier with which the tests were carried out. G is a glass container of about 5·5 litres capacity, in the floor of which is the cathode K, and in the cover the three iron anodes A, equally spaced in the form of a triangle. The cathode is shown in section in Fig. 2. The conical and cylindrical-shaped tungsten insertion-piece W is extended in an upward direction by a quartz cone Q, so that the arc may be ignited in it by touching the mercury with the ignition anode Z. After ignition, the mercury is lowered into the cylindrical part of the tungsten insertion-piece by rotating the screw S. When increasing the cathode current, the mercury pressure must be adjusted at the same time by means of the screw S, so that the surface of the mercury, which is entirely covered by the cathode spot, neither rises nor sinks. The pressure can then be read on the slanting capillary glass tube O. In order to determine the amount of mercury vapour, the decrease in the mercury level in the tungsten insertion-piece and the corresponding ampère-seconds were determined at a constant temperature of the container and with the mercury feed pipe closed. It is well known that the vaporization of mercury at the cathode of a mercury arc with a free moving cathode spot has already often been established.[2] When the cathode spot

[1] R. Tanberg, Phys. Rev. **35**, 1080 (1929).
[2] Zeits. f. Physik **2**, 74–87 (1922); Phys. Zeits. **29**, 857 (1928); Phys. Zeits. **30**, 233 (1929).

is moving freely, the surface of the mercury is much larger than the area of the spot, and in this case the vaporization is greatly dependent upon the mean temperature of the surface of the mercury. When the cathode spot is fixed and covers the entire surface of the mercury, the amount of vaporization remains at a certain value which is no longer greatly dependent upon

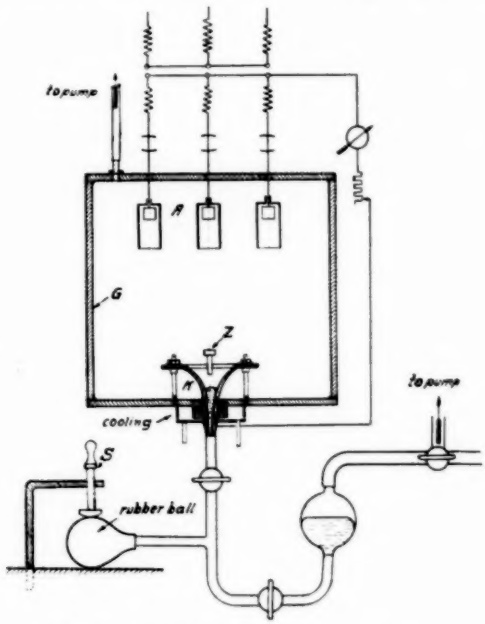

Fig. 1. Diagram of 3-anode rectifier.

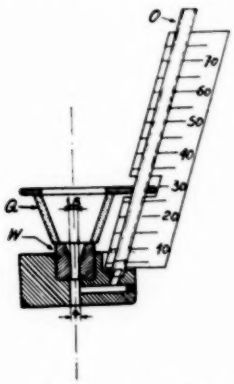

Fig. 2. Cross section of cathode.

the cooling of the cathode. This is also the case with a strongly-cooled copper-mercury cathode. The copper disk used as a cathode contained holes of about 2 mm diameter filled with mercury. A cooling liquid with a temperature of $-10°C$ was circulated round a channel in the disk during the test. The arc only burned until all the holes covered by the cathode spot were used up. A subsequent examination of the copper disk showed that it had been scarcely burned by the arc, since an arc current of only 14 amp. was used.

Results

The amount of mercury vapour at an average current of 35 amp. and with the cathode spot fixed in the tungsten insertion-piece was 0.017×10^{-3} gr/amp. sec.

The gas pressure in the container, arc current, force on the cathode spot and vapour velocity are given in Table I. The vapour velocity was calculated from formula (9) in Mr. Tanberg's article. No corrections for electrostatic and electrodynamic forces were made because they are of so little influence (less than 5 percent) that they do not effect the comparison of results which are already approximate.

Table I.

1	2	3	4	5	6
Arc current amp.	Current density in cathode spot amp./cm²	Gas pressure mm Hg $\times10^{-3}$	Height of mercury in glass tube cm	Force in dynes	$(C^2)1/2$ vapour ty in cm/sec.
30	1700	1	6.5	1470	42×10^5
37	2090	0.5	3.0	687	16
35	1980	1.5	6.5	1470	36
32	1810	0.5	7.0	1700	43

The figures in column 3 give only the gas pressure in the container, and not the mercury vapour pressure.

These values do not vary more than those of Mr. Tanberg. In the case of the above-described tests, the variation arises from the difficulty of adjusting the counter pressure of the cathode mercury. The close agreement of the results is of special interest considering the difference between the two methods of measurement. These results show that it is not possible to calculate the vapour velocity with a moving cathode spot; this velocity would be smaller but very variable. The well-known zig-zag movement of the cathode spot with mercury arcs is certainly due to the fact that the mercury transmits the pressure of the vapour to the sides of the vessel if the cathode spot is not held stationary.

Mr. Tanberg also calculates the absolute temperature of the cathode spot from the vapour velocity, and obtains a temperature of the order of 5 to 7×10^5°K. Mr. Compton[3] has since given us a new reason for the high vapour react. force, so that it is useless to calculate the temperatures from the velocities given here. On the other hand, the question arises why the amount of mercury vapour per amp. sec. in a mercury arc is the same as the amount of copper vapour in a copper arc. There appears to be some close relationship between the amount of cathode voltage drop and the thermal properties of the cathode material-specific heat, heat of fusion, heat of vaporization and heat-conductivity.

[3] K. T. Compton, Phys. Rev. **36**, 706 (1930).

PHOTOELECTRIC EMISSION FROM THIN FILMS OF CAESIUM

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(Received October 22, 1930)

Abstract

The photoelectric properties and the methods of preparing thin films of caesium are described. These are divided into two classes: (1) Those where a thin film of Cs is adsorbed on a thin layer of oxygen. (2) Those where a thin film of Cs is adsorbed on a layer of suboxides of Cs.

Surfaces of the latter type were prepared by coating a cathode with metallic caesium and then admitting oxygen in very small quantities. The photoelectric current was observed simultaneously. The measurements show that the most sensitive surfaces are obtained when the caesium has taken up sufficient oxygen to form a suboxide rather than the normal oxide Cs_2O. These films owe their properties to the arrangement of the molecules very near the surface.

RECENT workers[1,2,3] have described some of the photoelectric properties of thin films of alkali metals. The following investigation was directed particularly at the physical structure and chemical composition of such surfaces.

The first precise measurements of the properties of thin films of atomic dimensions of the alkali metals as distinguished from the bulk metals were made by Ives,[4] who also investigated the effect of the underlying material.

In this laboratory, Bainbridge and Charlton developed a method of obtaining thin very stable films of caesium giving high values of photoelectric emission. The method consisted in exhausting and silvering a photoelectric cell in the usual manner,[5] then introducing a fairly large amount of caesium into the bulb and again baking out the cell while still on the exhaust system at a temperature of about 300°C. During this bake-out, the photo-sensitivity of the cell increases, passes through a flat maximum and if the bake-out is continued sufficiently long or the temperature is sufficiently high, falls to a very small value. The maximum probably coincides with the formation of an adsorbed monatomic film of caesium on the surface of the silver. The excess of caesium distills out through the top tube into the exhaust system.

It was later found possible to make more uniform surfaces and more sensitive surfaces by first adsorbing a thin layer of oxygen on the silver. This was done by heating the bulb (after silvering) to 360°C, admitting a

[1] N. R. Campbell, Phil. Mag. **6,** 633 (1928).
[2] Olpin, Phys. Rev. **36,** 251 (1930).
[3] Zworykin and Wilson, Jr. Opt. Soc. **19,** 81 (1929).
[4] Ives, Astrophys. J. **60,** 209 (1924).
[5] Koller, Trans. Soc. Motion Picture Eng. **12,** 921 (1930).

few mm of oxygen and allowing the bulb to cool to room temperature before pumping out the gas. Caesium was then introduced and the cell treated as before. Surfaces formed in this way gave a spectral sensitivity curve as shown in Fig. 1. This type of cell will hereafter be referred to as Cs-O-Ag. The shape of the maximum at the edge of the ultraviolet is probably largely determined by the transmission of the glass. The curve, however, is radically

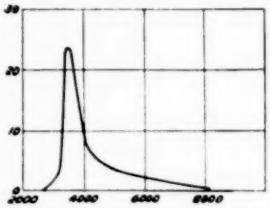

Fig. 1. Color sensitivity curve for Cs-O-Ag.

different from that determined for caesium in thick layers by Miss Seiler[6] which shows a maximum at 5500A. These Cs-O-Ag surfaces are very stable and are not appreciably affected by temperatures below 100°C.

Similar results have been obtained with potassium on oxidized copper by N. R. Campbell.[7]

That these films are of atomic dimensions was shown for the case of potassium as follows. A long glass capillary was sealed to a photo-cell of the usual construction as shown in Fig. 2. At the end of this tube was a bulb containing some redistilled potassium. The bulb and capillary were immersed

Fig. 2. Tube for determination of film thickness.

in an oil bath at a temperature of 155°C, while the photoelectric cell (still connected to the vacuum system) was maintained at room temperature. The quantity of potassium passing through the capillary per unit time was computed from Knudsen's formula

$$Q_2 = \frac{P_2 - P_1}{W_1(\rho_1)^{1/2}}$$

[6] Seiler, Astrophys. J. **52,** 1929 (1920).
[7] Campbell, Phil. Mag. **6,** 633 (1928).

where $P_2 - P_1$ is the difference in pressure between the ends of the tube; ρ_1 the density of gas at the temperature of the tube; $W_1 = 2.394l/D^3$ (l = length and D = diameter of tube); and Q_2 is the quantity of gas which flows through the tube per second.

The tube used was 10 cm long and 3 mm in diameter. The value for Q for these conditions was 3.62×10^{-8} gm/sec.

Since the area of the photo-cell was 170 cm^2, sufficient potassium to give a monatomic film would diffuse through the capillary in 2.5 minutes. Fig. 3 shows the change in sensitivity with time under these conditions. It passed through a maximum in 12.5 minutes. This was the time required for the deposition of a layer 5 atoms deep. As there is no reason for assuming the formation of a layer of uniform thickness over the entire bulb wall under these conditions the average thickness must have been of atomic dimensions.

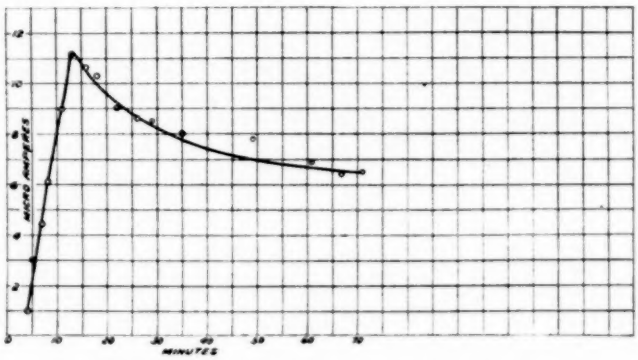

Fig. 3. Variation in photo current with time.

Cells were also made with a sheet of copper, plated electrolytically with silver as cathode. When treated as already described, this gave the same sensitivity as the evaporated metal deposit.

Throughout the discussion, unless otherwise specified, sensitivity will be taken to mean the response to the unresolved light of a tungsten filament lamp at 2400°K. Thus increasing sensitivity may be the result of an increase in the ordinates of any part of the spectral sensitivity curve or may be due to a lowering of the work function and consequent shift of the long wave limit toward the red.

When the oxidation of the silver cathode was carried out in such a manner as to give a layer of Ag_2O several hundred molecules deep, the results were radically different. If caesium was distilled into the tube and allowed to stand for a sufficiently long time, it gradually disappeared from the bulb walls and was completely absorbed by the silver oxide. It could be recovered again by very gentle warming of the plate. Such a surface shows only a very slight photo sensitivity. If the surface, however, is heated to temperatures in the neighborhood of 250°C, a reaction takes place and a compound is formed which is remarkably photo sensitive. Fig. 4 shows a spectral sensitivity curve for such a surface. Vacuum cells giving currents as high as 18

microamperes per lumen have been made in this way by Mr. H. E. Thomson who has done much of the development work in this field. This curve shows approximately the same maximum in the blue end of the spectrum as the Cs-O-Ag surfaces. Its high sensitivity is due to a pronounced maximum in the red and near infrared and a probable shift in the long wave limit toward the red.

These surfaces are very difficult to reproduce as their formation depends upon several factors which are not easily controlled. The silver oxide dissociates at 270°C. The amount of caesium condensed on the cathode depends upon the relative temperatures of the cathode and bulb wall, and consequently on the rate of heating and the masses of the various parts. In addition there is, of course, the problem of introducing definite small quantities of caesium. This type of surface owes its properties to the formation of a thick layer of oxides of Cs. The function of the silver is merely to provide an oxide which is readily reduced by caesium. This type of surface

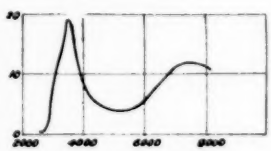

Fig. 4. Color sensitivity curve for Cs-CsO-Ag.

will be referred to as Cs-CsO-Ag. As will be shown later, the same results can be obtained with any base provided that the oxygen is introduced in the proper manner.

If the conditions during the exhaust of the cell were such that an excess of caesium remained in the bulb, the photosensitivity was invariably very low. On the other hand, if the heat treatment was continued so that the caesium was completely oxidized, the photo-sensitivity disappeared entirely. Apparently the optimum condition was a thin layer of caesium on top of a layer of caesium oxide. This condition could be arrived at, however, only when the oxide was formed by the reduction of Ag_2O by caesium. The normal oxide of caesium coated with a thin film of metallic caesium would not serve. Tubes were made up with a heavy deposit of caesium on the cathode, which was then completely oxidized, the oxygen was pumped out, and fresh caesium was distilled into the bulb. It was then sensitized in the usual way, but showed only the normal sensitivity for Cs-O-Ag.

Additional evidence in support of this view was obtained by making measurements of photo-sensitivity during the sensitizing bake-out. Since the photo-currents under these conditions are comparable with the thermionic currents[8] and leakage currents, the light source was chopped up by a sector disc (three 60° openings rotated at 2200 r.p.m.) and the current observed on a simple a.c. amplifier. This indicated only the a.c. due to the photoelectric current. It was found that under these conditions the photo-sensitivity

[8] Koller, Phys. Rev. **33,** 1082 (1929).

never appeared until the exhaust oven was raised and the cell began to cool down, when it rose to its maximum value very rapidly. This may be interpreted as meaning that during the bake-out caesium atoms which reach the cathode surface are at once converted to a non-photosensitive caesium oxide. It is only as the cathode cools that a photo-sensitive layer of metallic caesium is formed there.

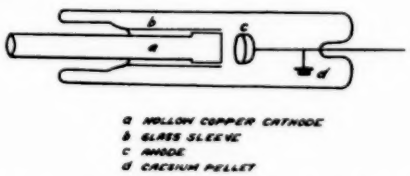

Fig. 5. Tube with water-cooled cathode for observing effect of oxygen.

In an attempt to explain these phenomena, the problem was attacked in a slightly different manner. A tube was constructed, as shown in Fig. 5, with a hollow cathode which could be water cooled. This cathode was sealed

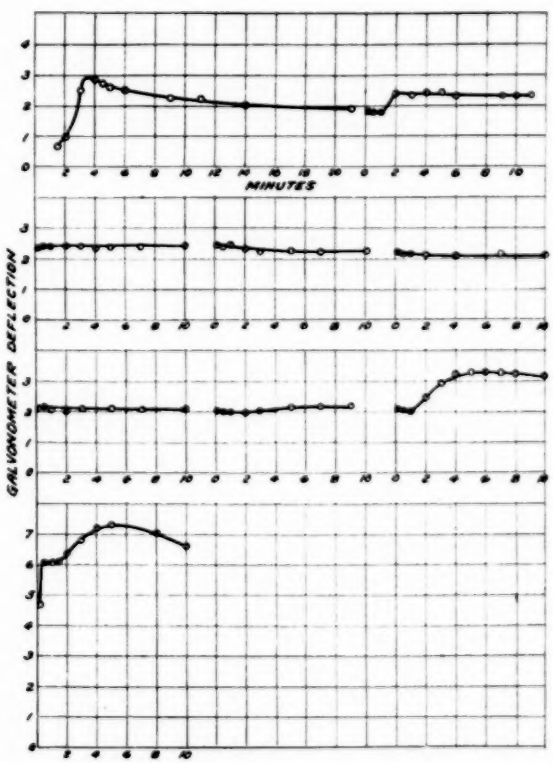

Fig. 6A. Effect on photo current of small "doses" of oxygen.

in by means of a chrome iron seal. A tight fitting glass sleeve covered the cathode so that only the end was exposed. The end of the cathode was a copper disk 3/4″ in diameter. The anode was a nickel ring 7/8″ in diameter spaced 1/2″ from the cathode. In the upper part of the bulb were several Ni

pellets containing a mixture of $Cs_2Cr_2O_7$ and Si from which caesium could be liberated by heating with a high frequency induction furnace. The tube was well baked out while exhausting. A liquid air trap was used and all measurements were made with the tube on the exhaust system.

Fig. 6 shows a typical set of measurements. With no caesium in the tube, the photo-sensitivity of the cathode was 0. The caesium pellet was flashed

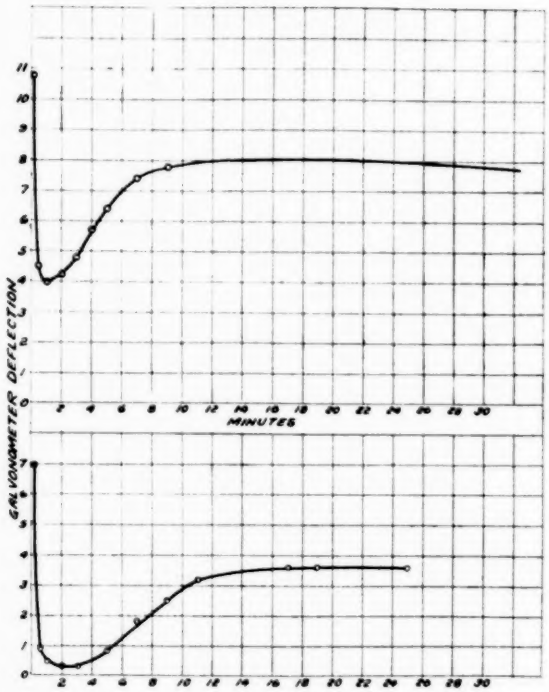

Fig. 6B.

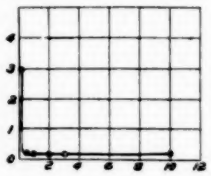

Fig. 6C.

and measurements of photo-sensitivity were made at frequent intervals. A stream of water was kept flowing through the cathode so that it was the coolest part of the bulb. The photo-sensitivity to unresolved light shows a fairly rapid increase with time, reached a maximum in about four minutes and eventually fell off to a constant value.

In about 20 minutes all of the caesium was condensed on the cathode. This was a thick visible deposit. Assuming 100 percent yield of caesium from the pellet, this was estimated to be 2×10^4 atoms thick. A small dose of

oxygen sufficient to fill the system to a pressure of 3.5μ was now admitted. As can be seen from the figure, this had no appreciable effect on the photo-sensitivity of the cathode. Measurements of pressure showed that the oxygen had been practically completely "cleaned up" by the caesium in the first three minutes. Successive doses of oxygen were admitted and photo-sensitivity and pressure observed. For the next six doses, the rate of clean up remained the same, and likewise the photo-sensitivity remained the same as for the clean caesium surface. The seventh dose, however, resulted in a 50 percent increase in sensitivity. The next dose also resulted in a large increase. The following dose, however, produced a strikingly different effect. The sensitivity passed through a maximum at least five times as large as the initial value within ten seconds of the admission of the oxygen, dropped to a low value and then gradually recovered. Additional doses of oxygen produced curves of similar shape but with a lower equilibrium value each time until finally all photo-sensitivity disappeared.

The maximum in the curve for pure caesium is of the right order of magnitude for the time required for sufficient caesium atoms to strike the surface to form a layer of atomic dimensions.

Once a thick layer of caesium is formed, small pressures of oxygen have no effect as the oxygen is absorbed as fast as it strikes the surface and the surface remains essentially a caesium surface. Finally a concentration of oxygen is reached, however, which corresponds very nearly to a suboxide of caesium. Under these conditions, the rate of absorption of oxygen is greatly reduced, the character of the final surface changes from a clean caesium surface to a composite surface consisting of atoms of caesium and oxygen. This is the condition represented by curves 7 and 8. Further doses of oxygen result in the formation of a layer containing the optimum amount of oxygen as represented by the peak in the curve, but this is rapidly destroyed by the excess of oxygen. The gradual recovery corresponds to a rearrangement of the surface as caesium diffuses out.

This experiment was repeated several times, always with the same results. In each case the amount of oxygen cleaned up corresponded to a suboxide of caesium. The oxygen could be measured to a high degree of accuracy, but there is always some uncertainty as to the yield from the pellet. The calculations were based on the assumption of 100 percent yield.

The experiment was now carried out under slightly different conditions. The same tube was used as before, but the oxygen, instead of being admitted in "doses," was allowed to flow into the tube continuously through a capillary leak. The rate of leak was made the same as the previously observed rate of clean up of oxygen, namely, 1μ per minute. After a thick film of caesium had been condensed on the cathode, the flow of oxygen was allowed to start through the capillary and measurements of pressure and photo sensitivity were made at frequent intervals.

The results are shown in Fig. 7. After the first minute the photo-sensitivity remained practically constant for twenty-six minutes when it began to increase, passed through a maximum and fell to zero. The amount of

O_2 which had been absorbed when the photo-sensitivity reached its maximum was 32μ, which is in good agreement with the amount determined by the discontinuous method. The pressure remained constant at 2.5μ throughout the experiment.

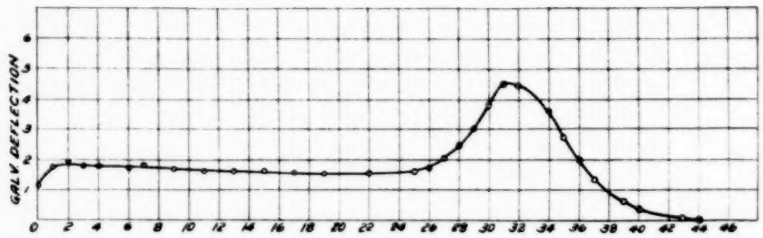

Fig. 7. Effect on photo current of small flow of oxygen.

$32/\mu$ corresponds to 82×10^{-6} gm of oxygen. Assuming that the yield of caesium was 9×10^{-3} gm, this gives a ratio of $Cs/O=110$. The ratio for Cs_2O would be 33.

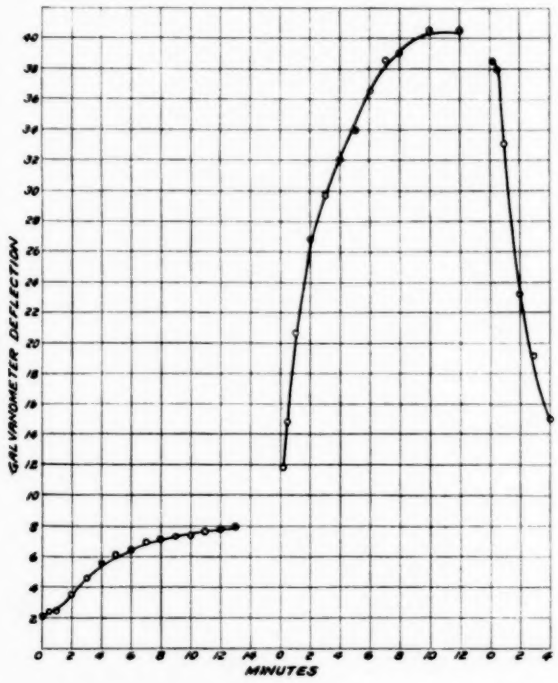

Fig. 8. Effect on photo current of small "doses" of oxygen at liquid air temperature.

The conclusion to be drawn from these experiments is that the highly photo-sensitive surface obtained by treating caesium with oxygen is due to a thin film of caesium upon a foundation of suboxides of caesium. If the caesium is present in large quantity, it must be entirely converted to sub-oxide before such a surface can be obtained. Until the entire amount of

caesium is oxidized, the process of diffusion maintains a practically clean caesium surface.

An experiment was undertaken to study such a surface in the absence of diffusion. The same tube was used as before, and after being thoroughly exhausted, the pellet was flashed. The cathode was then chilled with liquid air. Since the cathode was of heavy copper, the surface of caesium in contact with it was likewise at nearly liquid air temperatures. Fig. 8 shows the change in photo-sensitivity with time as the caesium condensed out upon it. This curve was very similar to the one obtained at room temperature. Oxygen was now admitted in very small doses, 0.6μ at a time. This quantity is sufficient to form a layer 6 atoms deep on the surface of the cathode. It is probable that some caesium remained on the bulb wall so that the first dose of oxygen may have been partly taken up elsewhere than at the surface of the cathode. The very first dose of oxygen now produced a four-fold increase in sensitivity, while the second dose raised the sensitivity to *twenty times* its initial value. This is in marked contrast with the effects at room temperature where fifty times this quantity of oxygen was required to produce an appreciable effect. The explanation lies in the fact that at the low temperature the oxygen cannot diffuse in, so that a very small amount can be effective in changing the surface structure. This experiment lends further support to the view that the chief function of the thick oxide layer in the Cs-CsO-Ag cells is to use up the free caesium so as to immobilize the surface layer.

THE MAGNETIC SUSCEPTIBILITY OF GASES II. TEMPERATURE DEPENDENCE

By Francis Bitter*

California Institute of Technology and Research Laboratories, Westinghouse Electric and Manufacturing Company

(Received October 20, 1930)

Abstract

The susceptibilities of CO_2, N_2 and H_2 are measured at room temperature and at liquid air temperature using O_2 as a standard. The results are:

Molecular susceptibility $\times 10^6$

	298°K	88°K
CO_2	−24.2	———
N_2	−14.8	−14.2
H_2	−5.8	−3.3

The relative values at room temperature are in fair agreement with most previous observations, but the absolute values are more diamagnetic than any previously recorded. The low temperature observation on N_2 can be interpreted as meaning that if a permanent moment is present, it is less than 1/25 of a Bohr magneton. The large change observed in H_2 is entirely unexpected, and the observations should be repeated.

IN A previous communication,[1] hereafter referred to as Part I, the proportionality between volume susceptibility of gases and pressure was established, thus clearing the way for an examination and interpretation of the temperature dependence. On the assumption that there is no diamagnetic orientation and that the molecular susceptibility of polyatomic gases is unaffected by temperature changes through such mechanisms as, for instance, slight differences in nuclear separations in various thermally excited states, the expression for the volume susceptibility may be written

$$K = \left(\frac{a}{T} + b\right)\frac{p}{T} \tag{1}$$

p and T stand for pressure and absolute temperature; a is a positive constant which measures the permanent moment of the molecule; b is a negative constant which measures the diamagnetism. The work described below is concerned chiefly with the gases O_2, H_2, and N_2. For O_2 b may be taken equal to zero, and in this form Eq. (1) has been tested[2] over a considerably range of temperatures and pressures and found to hold. For H_2 and N_2 it has heretofore been assumed that $a=0$, and it is the chief purpose of this paper to check this assumption, and to discuss the absolute values of the constant b.

* National Research Fellow.

[1] F. Bitter, Phys. Rev. **35**, 1572 (1930).

[2] K. Onnes and E. Oosterhuis, Konink. Akad. Wetensch, Amsterdam, Proc. **15**, 1404 (1913). Communication No. 134d from Phys. Lab. Leiden.

The Apparatus

The apparatus used in the following measurements is essentially the same as that described in Part I. A liquid air trap was introduced between the gasometer containing pump oil and the quartz furnace containing copper filings in order to prevent any vapors from reaching the furnace. Further, in order to reduce the volume of the purifying train, two of the three drying tubes were removed, leaving one tube containing P_2O_5 and the long spiral immersed in liquid air to accomplish the drying of the gases. The functioning of the train was checked spectroscopically as described in Part I.

Preliminary trials at low temperatures showed that the measuring apparatus described in Part I was not satisfactory. Even after the Dewar had been filled with liquid air and left standing for hours, the test body would not come to rest. This was due to slight convection currents, which were greatly reduced by enclosing the test body in a chamber of slightly different design as shown in Fig. 1. The resistance thermometer was eliminated

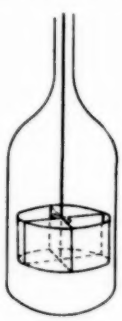

Fig. 1. Diagram of apparatus.

entirely. The container was immersed in liquid air up to the constricted portion. This was done by means of a Dewar flask which fitted between the pole-pieces of the magnet. In this way the test body was almost completely surrounded by walls at liquid air temperature, and heat was brought into the measuring chamber only along the long thin stem of the test-body. Further trials showed that this arrangement was satisfactory. The temperature was read on a pentane thermometer immersed in the liquid air bath. Its accuracy was first checked against the boiling point of pure O_2.

Theory of Measurements

Previous work had established the proportionality between, first, pressure and deflection of the test body; and second, pressure and volume susceptibility. From this, proportionality between deflection and susceptibility could be inferred for all measurements carried out at any given temperature. Thus if δO_2 and δH_2 represent the deflections produced by O_2 and H_2 at a pressure of say 1 cm, we may write

$$(K_{H_2})_{T,p} = \left(\frac{\delta H_2}{\delta O_2}\right)_T (K_{O_2})_{T,p} \qquad (2)$$

In the following, oxygen was used as a standard, it being assumed[3] that its volume susceptibility, K_{O_2} at 20°C and 76 cm pressure was 0.14×10^{-6}, and that its volume susceptibility at any other temperature T could be found by multiplying the above figure by $(293/T)^2$.

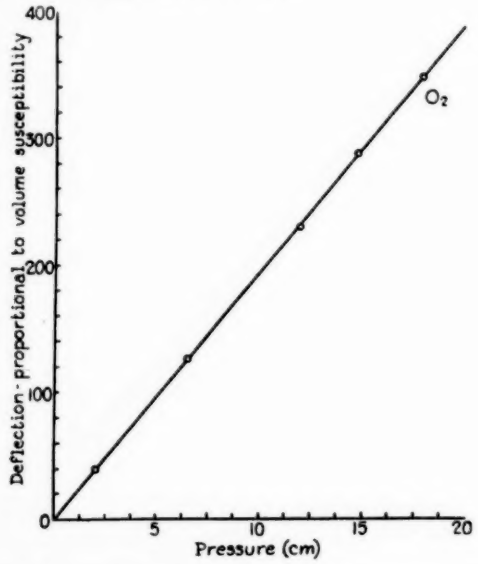

Fig. 2. Deflection, or volume susceptibility of O_2 in arbitrary units plotted as a function of the pressure, the observations being made at room temperature.

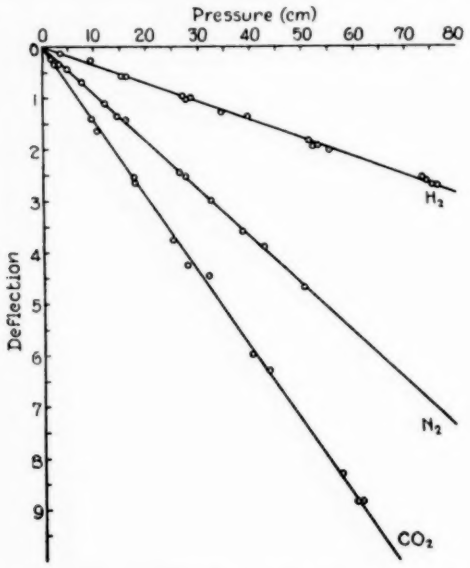

Fig. 3. Deflection or volume susceptibility of H_2, N_2, and CO_2 in the same units as those used in Fig. 2, plotted as a function of the pressure, the observations being made at room temperature.

[3] J. H. Van Vleck, Phys. Rev. **31**, 608 (1928).

In making a measurement the procedure was therefore the following: first plot the pressure vs. deflection curves, as in Figs. 2, 3, 4 and 5. From these obtain the quantities (δ_{H_2}) , and by substituting the numbers thus

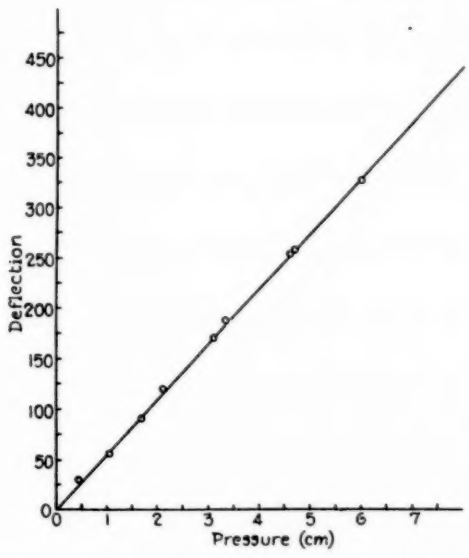

Fig. 4. Deflection, or volume susceptibility of O_2 in arbitrary units plotted as a function of the pressure, the observations being made at the temperature of liquid air.

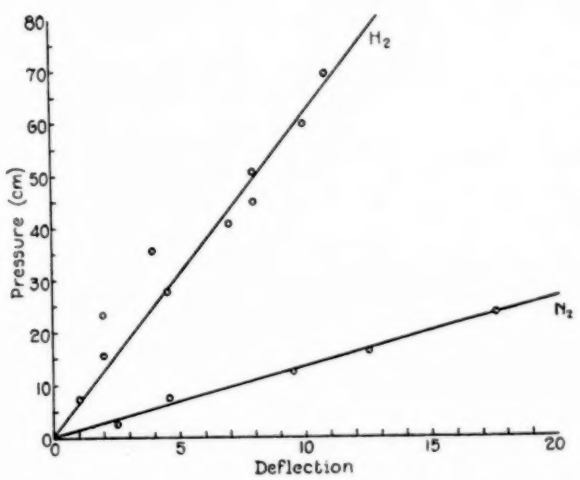

Fig. 5. Deflection, or volume susceptibility of H_2 and N_2 in the same units as those used in Fig. 4, plotted as a function of the pressure, the observations being made at the temperature of liquid air.

obtained into Eq. (2), the absolute values of the volume susceptibility at any temperature could be obtained.

Results at Room Temperature

As is evident from the above, these results may be divided into the following individual measurements: The ratio of the volume susceptibilities of a pair of gases; and the calibration, which involves the assumption of an absolute value for some standardizing substance. The division of the results into these two groups may conveniently be applied to the results of other observers, as most of their work has also been carried out in this fashion. Unless this is done, a faulty calibration would make all the measurements appear wrong, instead of showing up in the calibration as it ought. The results are shown in Table I.

Table I. *Ratios and absolute values of the molecular susceptibilities of diamagnetic gases as found by various observers. (Vaidyanathan did not measure H_2, but found an absolute value of -12.9×10^{-6} for N_2, which multiplied by 0.39 gives (-5.0) which for the sake of comparison, is listed above. All the measurements were carried out at room temperature.)*

	Hammar[4]	Wills & Hector[5]	Glaser[6]	Lehrer[7]	Vaidyanathan[8]	Také Soné[9]	Author
H_2/N_2	0.39	0.33	0.54	—	—	0.54	0.39
H_2/CO_2	.23	—	.22	.23	—	—	.24
N_2/CO_2	.59	—	.39	—	.63	—	.63
$H_2(\times10^6)$		−3.94	—	−5.0	(−5.0)	−3.94	−5.8

In the first part of the table, the agreement for H_2/CO_2 is good, and the value may be taken with considerable confidence as 0.23 ± 0.01. The next best is N_2/CO_2 where three of the four measurements point to 0.61 ± 0.02 as the correct value. The origin of the too low value for N_2 found by Glaser is not at all clear, and further work on this point should prove very interesting. Assuming that these two ratios are right, they give for H_2/N_2 $0.23/0.61 = 0.38$ in good agreement with the results of Hammar and myself (0.39). The agreement among the various absolute values for H_2 is very poor, and at present there seems to be no way of choosing the most nearly correct. I wish to add, however, that the use of the values for H_2 and N_2 found in this work would not invalidate the arguments advanced in an earlier paper[10] on the susceptibility of organic gases, where the measurements of Wills and Hector on N_2 and H_2 were used as standards.

Results at Liquid Air Temperature

For N_2 the ratio of the molecular susceptibility at 298°K to that at 88°K was found to be 1.04, which means that, within the experimental error, the

[4] G. W. Hammar. Thesis. California Institute of Technology. 1926.

[5] A. P. Wills and L. G. Hector, Phys. Rev. **23,** 209 (1924). L. G. Hector, Phys. Rev. **24,** 418 (1924).

[6] A. Glaser, Ann. d. Physik **75,** 459 (1924).

[7] E. Lehrer, Ann. d. Physik **81,** 229 (1926).

[8] V. I. Vaidyanathan, Phil. Mag. **5,** 380 (1928).

[9] Také Soné, Phil. Mag. **39,** 305 (1920).

[10] F. Bitter, Phys. Rev. **33,** 389 (1929).

susceptibility is expressible by an equation of the form $K=bp/T$. More accurately, it can be stated that if the N_2 molecule had a magnetic moment of 1/50 of a Bohr magneton, this would just have sufficed to change the above ratio from 1.00 to 1.04, and that hence, if the N_2 molecule does actually have a permanent moment, this is surely less than, say 1/25 of a Bohr magneton.

The result for H_2 is unexpected.

$$\frac{(\chi_{H_2})_{298^\circ K}}{(\chi_{H_2})_{88^\circ K}} = 1.82$$

This measurement involves considerable uncertainty, as is seen from the way the points are scattered about the line in Fig. 5. They represent data taken in two consecutive runs, and the difficulties in making accurate readings were due to unusually large random motions of the test body. It would have been highly advisable to repeat these observations, but this was impossible for lack of time. The above ratio is so large, however, that it is impossible to attribute it to any experimental error save that of O_2 contamination, which, in view of the precautions taken, seems out of the question. The result may therefore be stated by saying that at liquid air temperatures the molecular susceptibility of H_2 is only about half of its value at room temperature. Such an effect could be due to either an actual decrease in the size of the hydrogen molecule, or to an alignment of its axis parallel to the field in the ground state with no rotational energy. There seems to be no reason to expect either of these effects, even when the existence of a nuclear spin is taken into consideration. Future work on hydrogen should take into account possible differences between the para and ortho states.

THE MAGNETIC PROPERTIES OF CERTAIN Pt-Co AND Pd-Co ALLOYS

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(Received September 11, 1930)

Abstract

If ferromagnetism is due to interaction between the electrons of neighboring ferromagnetic atoms, the effect on the magnetic properties of gradually separating these atoms is of interest. For this reason alloys of the Pt-Co and Pd-Co series were investigated. As the alloys were solid solutions, for small cobalt content the cobalt atoms could be regarded as partly isolated by the non-ferromagnetic atoms. The magnetic properties of these alloys showed a lowering of the Curie point and a decrease in the remanent magnetization and coercive force with decrease in the percentage of cobalt in accord with theory. An observed increase in the magnetization per cobalt atom is discussed along with recent theories of ferromagnetism.

I. Introduction

THE explanation of ferromagnetism has presented much greater difficulties than that of either diamagnetism or paramagnetism. X-ray experiments on ferromagnetic crystals have shown that the elementary magnet cannot be larger than the atom, and the most recent work of Barnett[1] on the gyromagnetic effect indicates that ferromagnetism can be attributed chiefly to the spinning electrons. But in spite of the supposed simple character of the elementary magnet experiments have shed little light on its behavior in ferromagnetic substances.

The point from which to attack the problem of magnetism most directly would seem to be the Gerlach and Stern[2] experiments, in which the magnetic moment and behavior of an individual atom is measured. The sodium and cobalt atoms have been found to possess magnetic moments of one and six Bohr magnetons respectively, but in the solid state sodium is only paramagnetic while the magnetic moment per cobalt atom, computed for saturation magnetization, is about 1.7 magnetons. However, in the gaseous state of an atomic beam neither element can be classed as ferromagnetic. The fundamental question is what special mechanism in the solid state makes cobalt ferromagnetic and sodium not. Ferromagnetism arises only when certain atoms, (notably Fe, Ni or Co), are brought into the close proximity which they find in the solid state. This was first explained by Weiss as due to a large internal magnetic field set up by these atoms in the solid state, and the most recent theories have attempted to account for the mechanism by which this field is created. Heisenberg[3] deduces it from the resonance, (the "Austausch-

* National Research Fellow.
[1] S. J. Barnett, Phys. Rev. [2] **36**, 789 (1930).
[2] W. Gerlach and O. Stern, Zeits. f. Physik **9**, 349 (1922), etc.
[3] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928).

phänomene"), between the spinning electrons of neighboring atoms, while Bloch[4] believes the interaction takes place between the conduction electrons. It is therefore not surprising that ferromagnetism does not occur in liquids or gases where the separation of the atoms is greater. Further, as the orientations of the spinning electrons obeys a statistical energy distribution, the complicated nature of most ferromagnetic phenomena is accounted for, as well as the difficulty of using such measurements to work back to the mechanism of the individual atoms or electrons. Similar complications arise on the theoretical side, of a mathematical nature, and simplifying assumptions must be introduced, so that only predictions of a general character can be made.

In an attempt to simplify conditions it was thought interesting to observe the magnetic properties of ferromagnetic atoms in a state of isolation from one another intermediate between that of the pure solid metal and that of the Gerlach and Stern experiment. This suggested investigating alloys of a ferromagnetic with a non-ferromagnetic metal. By increasing the percentage of the latter the atoms of the former could be further and further isolated from each other and the corresponding effect on the magnetic properties noted. The present work is a continuation of that on the same subject previously reported by the author.[5]

2. Experimental Method

Several alloys of iron, nickel, or cobalt with other metals have been investigated. In nearly every case a small percentage of the non-magnetic element was sufficient to prevent ferromagnetism. For example, Lewkonja[6] has tested alloys of Co with Sn, Sb, Pb, Bi, Zn, Cd, Cr and Si and Tammann,[7] those of Fe, Ni or Co with Sn, Sb, Pb, Bi, Zn, Si, Al and Mg. In many cases, such as the Ni-Cr series,[8] the Curie point falls more and more rapidly to absolute zero as a few percent of, say, Cr is added. For Ni-Mn[9] it decreases steadily to 0°C for 25 percent Mn. But in all these cases it is doubtful whether the two metals concerned form a continuous series of solid solutions, such as would be necessary for the purpose of this problem in order that the ferromagnetic atoms could be gradually further isolated. For the Ni-Cu series,[10] however, the Curie point reaches −230°C for 65 percent Cu, and it is believed that these two metals are mutually soluble except for a small range around 50 percent Cu. But in the present work, alloys of cobalt have been selected in which the cobalt content can be made only a few percent without complete loss of ferromagnetism; these alloys belong to the Pt-Co and Pd-Co series. Although the diagram of thermal equilibrium has not been obtained for either of these series, Carter has investigated many high platinum alloys and believes platinum and cobalt to form an isomorphous series of solid solutions. As previous-

[4] F. Bloch, Zeits. f. Physik **57,** 545 (1929).
[5] F. W. Constant, Phys. Rev. [2] **34,** 1217 (1929).
[6] K. Lewkonja, Zeits. f. anorg. Chem. **59,** 293 (1908).
[7] G. Tammann, Zeits. f. phys. Chem. **65,** 73 (1909).
[8] C. Sadron, Comptes Rendus **190,** 1339 (1930).
[9] S. Kaya and A. Kussmann, Naturwissenschaften **17,** 995 (1929).
[10] R. Gans and A. Fonseca, Ann. d. Physik [4] **61,** 742 (1920).

ly reported,[11] a microscopic investigation was made on each alloy used, confirming Carter's conclusions. Similar results were obtained for the Pd-Co alloys.

The first set of alloys investigated was the following, kindly supplied in the form of 30 mil wires by the Bell Telephone Laboratories:

10% Co—90% Pt
5% Co—95% Pt
10% Ni—90% Pt
5% Ni—95% Pt

The magnetic properties of these alloys have already been reported. The last two were not ferromagnetic, and the results obtained from the first two will be summarized below.

A second set of alloys was prepared, in the form of 10 mil wires whose compositions by weight were the following:

3% Co—97% Pt
1.5% Co—98.5% Pt
10% Co—90% Pd
5% Co—95% Pd

The first two alloys served as a continuation of the Pt-Co series, while in the last two palladium was substituted for platinum so that by comparison with the Pt-Co series the contribution to the magnetic behavior of the cobalt atoms alone might be more truly ascertained. The experimental method was the same as that used with the first set of alloys, the magnetic measurements being made by the ballistic method, with two identical rings connected differentially. Measurements were taken on (1) the variation of the magnetization, I, (magnetic moment per unit volume), with temperature, and the Curie point, (2) hysteresis loops between various maximum values of the applied magnetic force, H, and at different temperatures, and (3) the initial curve of magnetization for various fixed temperatures. For the higher temperatures, (50°C to 350°C), turpentine or paraffin baths were used, while for lower temperatures the specimens were placed in a Dewar flask containing liquid air or a bath of ether cooled by liquid air. Temperatures were measured by copper-constantan thermocouples.

The alloys were first tested in the hard-drawn state, when a microscopic examination showed the individual crystals greatly distorted and elongated; the wires were then annealed for three hours in a vacuum at about 1050°C, and afterwards allowed to cool gradually. The furnace was a small electric one, built by A. Goetz, consisting of two concentric cylindrical crucibles with between them the heating element, a slightly conical helix of tungsten wire which served as a thread in which the inner crucible could be tightly screwed. After annealing the wires appeared microscopically to be composed of much larger crystals forming a polygonal pattern, characteristic of solid solutions.

[11] F. W. Constant, Phys. Rev. [2] **35**, 116 (1930).

3. Results and Discussion

The results for all the alloys in both the hard-drawn and annealed states are summarized in Tables I, II, and III.

Table I. *Curie Point.*

Alloy	% Cobalt			Curie Point,° Kelvin	
	by Wt.	by Vol.	Atomic	Hard-drawn	Annealed
90% Pt	10.0	21.4	26.9	578	522
95% Pt	5.0	11.4	14.9	322	322
97% Pt	3.0	7.1	9.3	193	179.5
98.5% Pt	1.5	3.7	4.8	—	87.5
90% Pd	10.0	13.4	16.8	511	462
95% Pd	5.0	6.8	8.7	359	301

In Table I are given the percentages of cobalt in each alloy by weight, by volume and from atomic considerations. The Curie points follow. For both series of alloys, in passing from 100 percent Co, with Curie point = 1388°K to 0

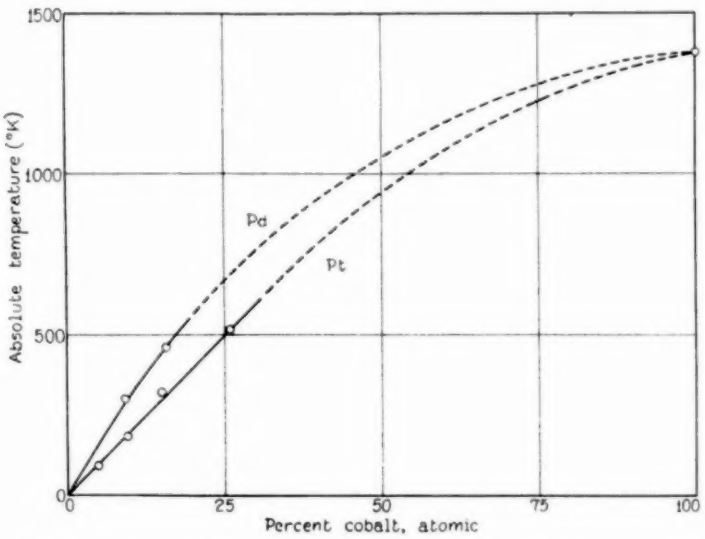

Fig. 1. Curie point as a function of the atomic percentage of cobalt.

percent Co, the Curie point decreases more slowly at first and then falls approximately linearly with the atomic percentage of cobalt, approaching absolute zero for 0 percent Co. This is shown in Fig. 1. In the magnetization *–vs.–* temperature curves the magnetization at first increased with rising temperature, later falling to zero at the Curie point. This initial rise was explained as due to lack of saturation for the values of H that could be applied.

Table II gives the characteristics of various hysteresis loops, the coercive force, H_c, and the remanent magnetization I_r, where H_{max} is the limiting value of H for the loop.

TABLE II. *Coercive force and remanent magnetization.—190°C.*

Alloy	H_{max}	H_c Hard	H_c Annealed	I_r Hard	I_r Annealed
90% Pt	260	—	30	—	189
95% Pt	260	90	18	200	107
97% Pt	260	80	14	73	53
98.5% Pt	260	30	0	1	0
90% Pd	260	120	110	—	142
90% Pd	650	420	115	210	167
95% Pd	260	50	88	—	83
95% Pd	650	410	110	145	108

The effect of annealing is seen to be to lower the Curie point and to decrease the magnetic hardness and hysteresis; the mechanical hardness was simultaneously decreased. This intimate connection between magnetic and mechanical hardness is in agreement with McKeehan's[12] theory of magnetostriction. O. v. Auwers and Sizoo[13] have found that increasing the grain size by annealing produces just such results as these.

Decreasing the cobalt percentage always lowers the Curie point, and decreases H_c and I_r. As the hysteresis decreases the loops become less upright and more inclined, and for the 98.5 percent alloy, annealed, no hysteresis was observed. This is in complete accord with the recent resonance theories of ferromagnetism, for if residual magnetism and hysteresis are explained as due to interaction between neighboring spinning electrons this interaction must diminish and the Curie point fall as these electrons become less dense. Comparison between the platinum and the palladium alloys shows similar results for both series except that H_c is greater for the latter. The Pt or Pd atoms therefore seem to influence the hardness only and the ferromagnetism appears to be attributable to the cobalt atoms. It is of course possible that both Pt and Pd atoms contribute to the ferromagnetism in the same manner and degree but this seems less likely.

TABLE III. *Maximum values of I and the magnetic moment per cobalt atom.*

Alloy	I_{max} Hard	I_{max} Annealed	$I_{0,\infty}$ Annealed	$\sigma_a \times 10^{-20}$
90% Pt	330	364	392	2.11
95% Pt	230	254	290	2.83
97% Pt	105	126	132	2.09
98.5% Pt	8	8	9	0.30
90% Pd	223	318	356	2.96
95% Pd	193	216	274	4.46
			1 Bohr magneton $= 0.92 \times 10^{-20}$	

In Table III the second and third columns give the greatest values of I measured for each alloy. In most cases the greatest values of H which could be applied, namely, 600 to 1000 gauss, were not sufficient to produce saturation, but the approach toward saturation followed closely, especially in the case of the palladium alloys, the formula given by Weiss and Forrer,[14]

[12] L. W. McKeehan, Phys. Rev. [2] **26,** 274 (1925).

[13] O. v. Auwers and G. J. Sizoo, Zeits. f. Physik **60,** 576 (1930).

[14] P. Weiss and R. Forrer, Ann. d. Physique [10] **12,** 279 (1929).

$$I_H = I_\infty\left(1 - \frac{a}{H}\right)$$

where I_H is the intensity of magnetization for a magnetic force H, I_∞ the magnetization at saturation, $(H=\infty)$, and a a constant for a given alloy and temperature. Table IV shows how closely the values of I observed for the 10 percent Pd alloy fit those calculated from the formula

$$I_H = 356\left(1 - \frac{131.4}{H}\right)$$

TABLE IV. *Approach to saturation for 90% Pd—10% Co alloy.*

H	I calc.	I obs.
270	182	190
361	226	225
450	252	252
564	273	272
700	289	289
767	295	295
903	304	304
∞	356	—

In this way values of I_∞ were computed at two different temperatures, that of liquid air and that of solid CO_2 and alcohol. They were very nearly the same; if not, the value of I_∞ at absolute zero, $I_{\infty,0}$ could be calculated by the Weiss[14] formula for temperature dependence,

$$I_{\infty,T} = I_{\infty,0}(1 - AT^2)$$

where A is a constant and T the absolute temperature. Recently Bloch[15] has obtained a closely similar formula from his theory of ferromagnetism; namely,

$$I_{\infty,T} = I_{\infty,0}\left[1 - \left(\frac{T}{\theta}\right)^{3/2}\right]$$

where $\theta \doteqdot T_c$, the Curie point. In agreement with this formula, $I_{\infty,T}$ showed greater dependence on T with those alloys whose Curie points were lowest. The fourth column of Table III gives the values computed for $I_{\infty,0}$ and the fifth these values divided by the number of cobalt atoms per cc, i.e. the magnetic moment per cobalt atom, σ_a, assuming the magnetization is entirely due to the cobalt. For pure cobalt σ_a is only about 1.6×10^{-20} so that as the cobalt content decreases to 5 percent σ_a increases, while for still further dilution it appears to decrease. This might be explained on Bloch's theory, according to which the spinning electrons between which resonance occurs are free conduction ones rather than associated with definite atoms. This electron gas can show ferromagnetism only if it is not completely degenerate so that its electrostatic energy may exceed its zero-point energy, (on the Sommerfeld theory). If decreasing the cobalt content in these alloys decreases the density of these free electrons the zero-point energy would decrease and this

[15] F. Bloch, Zeits. f. Physik **61**, 206 (1930).

might account for the increase in magnetic moment. At the same time, due to the lessening of the electrostatic energy a point would finally be reached where ferromagnetism would no longer be possible.

The theory of Bloch was prompted by the work of Dorfman, Jaanus and Kikoin[16] on the change in atomic specific heat at the Curie point. Stoner[17] has recently reported an important change in their results which alters the conclusion drawn from them that ferromagnetism is due to conduction electrons. But it is hard to distinguish between conduction and orbital electrons, and the peculiar electron arrangements in the Fe, Ni and Co atoms would seem to be the most likely source of the ferromagnetism of these metals. It is probable that greater values of σ_a would have been obtained with the 3 percent Co and 1.5 percent Co if the Curie points of these alloys had not been so low that measurements could only be taken a little below them.

In conclusion the following suggestions, along the lines of McKeehan's[18] theory of ferromagnetism, are offered. Ferromagnetism occurs in certain metals only because in these metals the electrons are so arranged that resonance arises and the spins are oriented. Magnetic hardness arises because a change in the magnetization, or distribution of the spins, produces atomic magnetostriction, and hence gross magnetostriction unless the atomic magnetostriction of some of the atoms is of opposite sign so that compensation occurs. Such mechanical effects must be considered as partly influencing the degree of magnetization possible. As the percentage of non-magnetic or non-magnetostrictive atoms increases, the atomic magnetostriction per cobalt atom can increase for a given gross magnetostriction. Assuming the magnetostriction of these alloys to be the same as for cobalt this would mean a greater observable magnetic moment per cobalt atom, as each cobalt atom in the alloy would be more free, with increasing dilution, to take up its state of greatest possible magnetization, than in pure cobalt. However, too great dilution of the cobalt would prevent ferromagnetism from occurring.

The writer wishes to thank the National Research Council for its support, and Professor R. A. Millikan for his kind help and for the facilities of the Norman Bridge Laboratory.

[16] J. Dorfman, R. Jaanus and I. Kikoin, Zeits. f. Physik **54,** 277, 289 (1929).
[17] E. Stoner, Nature **125,** 973 (1930).
[18] L. W. McKeehan, reference 12.

THE MAGNETIC ISOTROPY OF A PARAMAGNETIC ALUM

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(Received October 20, 1930)

Abstract

It is shown that cubic crystals of potassium chromium alum are magnetically isotropic.

J. Forrest,[1] in 1926, was led from both theoretical and qualitative experimental grounds to the conclusion that a number of crystals had variations in the magnetic susceptibility with direction of the applied field which were not in strict accord with the Thomson-Voigt symmetry relations. In order to test this conclusion, measurements were made by the author on large single crystals of copper,[2] and it was found that there was no variation in the susceptibility greater than 1 percent. Copper is a diamagnetic material, and its magnetic properties are supposed to be mostly due to the Larmor precession of its closed shell of electron orbits. The theoretical basis on which Forrest was led to expect the anisotropies in question was derived from the use of a model consisting of elementary magnets fixed to points of a space lattice. It therefore seemed desirable further to test Forrest's conclusions using some paramagnetic substance, whose magnetic properties would be determined chiefly by incompleted shells of electrons, and would thus more closely approximate the theoretical model.

There are several paramagnetic alums with a cubic structure which can easily be obtained in large crystals suitable for this. Potassium chromium alum—$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$—was chosen for this purpose. Crystals were grown from saturated solutions of the pure salt by suspending small seed crystals in them. Two of these were ground into cylindrical shape for measurement, one having as the cylinder axis a <100> axis of the crystal, the other a <111> axis. The following were their dimensions.

Axis of cylinder	length	diameter
<111>	0.610 cm	0.686 cm
<100>	0.444	0.549

The structure of chrome alum has been determined by Vegard and Schjelderup,[3] who place the chromium atoms on a face-centered cubic lattice. The magnetic susceptibility per unit mass is given in the International Critical Tables[4] as 11.5×10^{-6}.

Measurements of the variation of the magnetic susceptibility were made with the apparatus previously described by the author.[2] Values of the susceptibility in arbitrary units were obtained for every 15° in the plane perpendic-

[1] J. Forrest, Trans. Roy. Soc. Edinburgh **54**, 601–701 (1926).
[2] C. G. Montgomery, Phys. Rev. [2] **36**, 498–505 (1930).
[3] L. Vegard and H. Schjelderup, Ann. d. Physik [4] **54**, 146–164 (1917).
[4] International Critical Tables VI, p. 360.

ular to the axis of the cylinder. These relative values of the susceptibility were analyzed in a Fourier series in terms of the azimuth ϕ, the angle between the field and an arbitrary polar axis in the plane of the base of the crystal cylinder. This gave the following results:—

$$\chi_{<100>} = 85.85 + 2.32\cos\phi - 0.34\cos 2\phi - 1.36\cos 3\phi + 0.12\cos 4\phi + 9.05\sin\phi + 2.71\sin 2\phi + 1.29\sin 3\phi - 0.45\sin 4\phi$$

$$\chi_{<111>} = 166.68 + 1.34\cos\phi + 0.18\cos 2\phi + 0.11\cos 3\phi + 0.42\cos 4\phi + 3.81\sin\phi + 0.27\sin 2\phi + 0.72\sin 3\phi - 0.38\sin 4\phi$$

These two runs were not made at the same sensitivity of the apparatus, and hence corresponding coefficients in the two series should not be compared. As in the previous work, the terms with the 360° period are to be ascribed to an instrumental error and should be ignored in the interpretation of the data. About a <100> axis, we should expect, if the crystal were other than isotropic, at least one large coefficient in the terms in 4ϕ. It is seen that the coefficients of these terms are much smaller than the coefficients of the 2ϕ and 3ϕ terms. These latter terms can have no physical significance, in view of the symmetry of the crystal. Hence we can assign none to the terms in 4ϕ. In a similar way, for the <111> axis, the 3ϕ term is small compared with the 2ϕ and 4ϕ terms. Thus we must conclude that chrome alum, as well as copper, forms magnetically isotropic crystals.

It remains to give an explanation, if possible, for the fact that Forrest obtained experimental evidence of some anisotropy in his crystals. Forrest gives a curve[5] showing the dependence of the intensity of magnetization parallel to the field upon the direction of the field in the $\{100\}$ plane, for ammonium iron alum—$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$. The curve drawn shows a four-fold symmetry. This substance is identical in structure with chrome alum, and would be expected to behave magnetically in the same way. If we measure off in this figure the radius vectors of the experimental points, and subject them to a Fourier analysis, as above, we obtain the following result in centimeters:—

$$I_{11} = 2.469 - 0.033\cos\phi - 0.018\cos 2\phi - 0.089\cos 3\phi + 0.072\cos 4\phi + 0.000\sin\phi - 0.048\sin 2\phi + 0.041\sin 3\phi + 0.029\sin 4\phi.$$

We see that here the terms in 3ϕ have a larger amplitude than the terms in 4ϕ, and we conclude that to draw a curve through these points which shows a four-fold symmetry is not justifiable. The explanation of Forrest's curves for the transverse component of the intensity of magnetization is not evident. It should be pointed out, however, that if these curves represent real effects, there should be a dependence of the susceptibility of the material upon the strength of the field, an effect which has not been observed.

In conclusion, the author wishes to express his thanks to Professor L. W. McKeehan for much helpful discussion, and to the Sterling Fellowship Fund for financial support.

[5] J. Forrest, reference 1, p. 615, outer curve, Fig. 1.

A METHOD FOR GROWING LARGE CRYSTALS OF THE ALKALI HALIDES

By John Strong

University of Michigan

(Received August 13, 1930)

Abstract

F. Stöber was specified four conditions which must be fulfilled in order to grow large crystals from fused salts. Ramsperger and Melvin in applying Stöber's method encountered difficulty. They were able to grow large crystals which, however, broke upon cooling on account of unequal temperature contraction of the crystal and the melting pot as well as on account of strains caused by unequal temperature contraction throughout the crystal.

Two new supplementary conditions are specified which together with Stöber's conditions give a method for growing alkali halide crystals in cylindrical form 4.5 inches tall by 4.5 inches in diameter.

THE alkali halides are very transparent to infrared radiations. Rock salt (NaCl) is transparent to all infrared radiations from the red out to wave-lengths of 15μ, sylvine (KCl) is transparent out to wave-lengths of 22μ, and potassium bromide (KBr) to 30μ. No data are available for potassium iodide (KI) but one would expect it to be transparent even further than potassium bromide since its restrahlen lies deeper in the infrared.

Professor H. M. Randall, Director of the Physical Laboratory at the University of Michigan suggested to the author, the importance of these salts as possible materials from which to make windows and dispersing prisms for use in infrared spectroscopy and supported the undertaking to develop a method of making crystals sufficiently large for these purposes.

The method of growing crystals of the alkali halides as described in this paper is similar to a method described by P. W. Bridgman[1] where a mold containing the molten salt is slowly moved from the interior of a furnace maintained above the melting temperature to an external colder region. By the method described in this paper an iron pot is filled with the alkali halide and heated in a furnace in such a way that the temperature field moves instead of the pot. The molten salt is cooled in such a way that solidification starts at the bottom of the pot and proceeds upward.

This method of growing salt crystals has been made the subject of a paper by F. Stöber.[2] In this paper Stöber laid down several conditions which must be satisfied in order that the method yield large flawless crystals. These conditions may be summarized as follows:

1. The crystallization must start at a single point on the bottom of the container. If this condition is not satisfied more than one crystal may be formed in the pot.

[1] P. W. Bridgman, Proc. of the Amer. Acad. of Arts and Sciences **64,** #2 December (1929).
[2] F. Stöber, Zeits. f. Kryst. **61,** 299 (1925).

2. There must be a strong vertical temperature gradient in the molten salt. This helps to keep the crystal properly oriented and prevents twinning.

3. Isothermal surfaces within the pot must be nearly horizontal to prevent convection currents in the molten salt. The melting temperature isothermal surface must be raised up through the molten salt slowly and uniformly so that the crystal laid down below this surface will be sound and flawless.

Ramsperger and Melvin[3] have applied the above principles with some measure of success but they were not able to make large crystals on account of the strains introduced by the heavy dishes used. They have attempted to get around this difficulty by using extremely thin walled crucibles made out of especially ductile platinum. In spite of this, however, they did not succeed in making sodium chloride crystals larger than one or two cm on an edge. They state, "All of these conditions are easily met and for all of the crystals which we prepared, we found that the entire contents of the dish became one large single crystal, but that in some cases this crystal broke along cleavage planes into several small crystals when the cooling was practically complete."

This experience of Ramsperger and Melvin has been found to agree with that of the author and as a consequence, two new conditions are added to those laid down by Stöber. When all five of these conditions are fulfilled, the preparation of large crystals is achieved without further difficulty.

A strong temperature gradient of 5.0 to 10.0°C per cm is maintained through the salt during the crystallization process. Thus, after the crystal is formed the top will be at a higher temperature than the bottom. When the crystal is slowly cooled to room temperature, the top is cooled through a greater temperature range than the bottom by about 100°C. This means that the contraction of the upper part of the crystal will be greater than that of the lower part—in other words, the crystal will be in a condition of strain.

It so happens that the alkali halides are quite plastic at high temperatures. If the equalization of temperature occurs when the crystal is plastic it will not break when cooled to room temperature. This is the basis for the first of the supplementary conditions to be fulfilled.

4. After the crystal has been formed and while it is still plastic, the bottom and top of the crystal must be brought to the same temperature in order that no strains will be introduced due to unequal contraction upon cooling to room temperature.

The last condition to be fulfilled is,

5. The crystal must be removed from the container before the cooling process begins in order to eliminate the strains introduced by the temperature contraction of the melting pot.

For the fulfillment of these conditions, an electric furnace was developed. The nickel resistor of the furnace was one arm of a self balancing Wheatstone bridge, and the furnace was heated by the bridge current. The resistor was wound around an alundum tube seven inches in diameter which is represented in Fig. 1. The resistor, as well as the melting pot, was protected from oxidation by an atmosphere of hydrogen within the furnace. Self-balancing was

[3] Ramsperger and Melvin, J.O.S.A. **15**, 359 (1927).

effected by changes in the bridge current resulting in changes of furnace temperature and consequently furnace resistance. The furnace in this manner, either held a temperature constant to 1/10°C or changed its temperature at a uniform rate depending on whether the other resistances of the bridge were kept constant or gradually changed. During crystal growth the furnace temperature dropped about 10° per day.

The accompanying figures show in a diagrammatic way the conditions existing at three important stages of crystal growth. In Fig. 1, we have a representation of the conditions in the furnace during crystal formation. Heat flows from the hottest region of the furnace to the cooler regions by way of the molten salt and metal cooler. The dotted lines indicate how the isothermal surfaces in the molten salt are probably distributed. The rod attached to the bottom of the pot insures that this point in the pot is coolest and, therefore, it is at this point that crystallization will start. The thick metal cooler

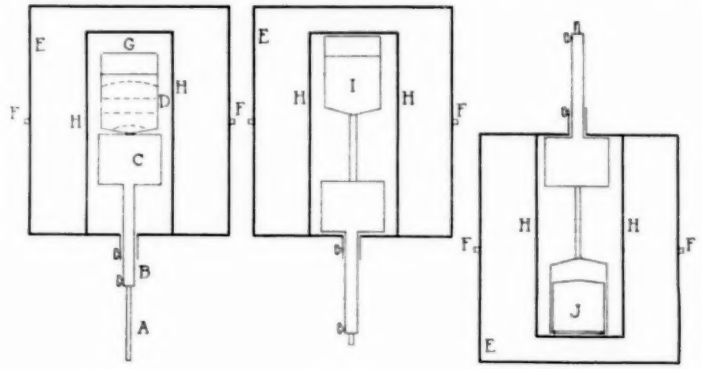

Fig. 1. Fig. 2. Fig. 3.

Diagrammatic representation of crystal growing furnace at three important stages of crystal growth.

A—Stem to raise or lower melting pot.
B—Sleeve to raise or lower metal cooler.
C—Metal cooler.
D—Dotted lines show probable isothermal surfaces. The melting temperature isothermal surface defines the boundary between crystal and molten salt.
E—Silocell heat insulation.
F—Axle for inverting furnace.
G—Lid to melting pot.
H—Alundum tube with nickel resistor.
I—Crystal at uniform temperature throughout.
J—Crystal free from melting pot.

immediately below the melting pot carries heat away from the bottom of the pot and insures the existence of a suitable temperature gradient. This metal cooler is movable from outside the furnace and may be adjusted to obtain the proper temperature gradient. As the furnace is gradually cooled the melting point isothermal surface moves up through the molten salt leaving a clear single crystal behind.

After the crystal has been formed the temperature gradient is removed by lowering the metal cooler and raising the pot until thermocouples at the top and bottom of the pot show equality of temperature throughout the crystal. At this time a slight plastic deformation occurs within the crystal but since this operation takes place at a temperature immediately below the melting point where the salt is quite plastic, no cracking occurs. This stage of crystal growth is illustrated by Fig. 2. In Fig. 3, we have a representation of the conditions existing just after the crystal has been melted out of the pot. When the temperature of the crystal has been equalized, the furnace is inverted and everything is then in readiness for the removal of the crystal from the pot. The furnace is strongly superheated for such a time as is necessary to melt the crystal away from the pot walls. A dull thud may be heard when the crystal drops onto the pot lid. This lid on to which the crystal drops is loose fitting so that the melted salt may run out of the pot. It is also corrugated so that it will catch and hold the crystal without causing it to suffer strains upon cooling due to unequal rates of contraction of the lid and crystal.

After this, it only remains to cool the crystal to room temperature which should not be so rapid as to cause cracking due to temperature contraction. For a single crystal weighing eight pounds, thirty hours time is sufficient for this cooling.

Large single crystals of cylindrical form have been prepared by this method ranging in size up to 4.5 inches tall by 4.5 inches in diameter. If the materials used are not pure a cloudiness will appear at the top of the crystal. Sometimes the top of the crystal is not clear because the temperature gradient at the top was insufficient. This cannot be conveniently avoided in the present form of the apparatus. Nevertheless, crystals have been made in the above size which are uniformly solid throughout.

Polished surfaces of potassium bromide and potassium chloride show less tendency to cloud than rock salt, when exposed to atmospheric moisture. A polished potassium bromide plate which has been exposed to room air for over two months shows no trace of reaction with the moisture in the air. Potassium iodide surfaces are less satisfactory in this respect yet they may be kept bright with sufficient care.

In conclusion the author wishes to acknowledge the skillful asistance of Mr. Paul Weyrich in making this undertaking a success.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Use of the Pierce Acoustic Interferometer

In the October 1 number (Phys. Rev. **30,** 1262, 1930) appears a letter by Elias Klein and W. D. Hershberger in which the writers claim that they do not consider the determination of the absorption coefficient in gases for high frequency sound by the Pierce acoustic interferometer method justified. I wish to repeat the cautions in the use of this method which I stated in my articles on the subject. (Phys. Rev. **34,** 1184, 1929 and Phys. Rev. **36,** 1005, 1930). I published my interferometer data in connection with absorption because the reactance and decrement of the plate circuit apparently played but a small part at 1200 kilocycles; also because simultaneous absorption and velocity determinations are desirable. The values for A by the interferometer and by the pressure vane methods agree with each other better than do many other independently measured acoustic determinations. Correspondence with the above writers revealed the fact that their letter was intended as a caution to others, particularly those contemplating the use of this method at lower frequencies.

In Phys. Rev. **35,** 814, 1930, Charles D. Reid reports an unequal spacing of maxima and what might be termed an acoustic backlash of 0.48 mm, apparently at a frequency of 42 kilocycles per sec. The unequal spacing confirms my findings as published in Phys. Rev. **34,** 1184, 1929 but I find the acoustic backlash, six wave-lengths from the crystal, to be less than 0.01 mm. ($\lambda = 0.0282$ cm; $\nu = 1219$ kc/sec.) The backlash or shift reported by Reid may be due to a persistance of resonance beyond the most favorable point in either direction.

W. H. PIELEMEIER

Pennsylvania State College

November, 1930

Wave Mechanics of Deflected Electrons

In the recent discussion[1] concerning the influence of quantum mechanics upon observations of e/m the actual method of experiment has not been analyzed very closely. In practice[2] an electron is caused to pass, first along a straight line through crossed electric and magnetic fields, then a further distance D through the same magnetic field alone. In the crossed fields we have, $eE = eHu$, whereas during the second part of its flight the electron is laterally displaced an amount (H and u being assumed small for simplicity) given by, $\delta = (eHu/m)\ (D^2/u^2)$; then $e/m = E\delta/H^2D^2$.

Now in the writer's paper[3] cited by Dr. Eckart it is shown that the center of a wave-packet for a free electron in a uniform magnetic field revolves in a circle at the classical angular rate eH/m. The packet must therefore undergo the classical acceleration eHu/m where u is the speed of motion of the packet along the circle. Similarly, in a uniform electric field the packet experiences the classical acceleration eE, superposed upon its quantum spreading. Accordingly the center of the packet should follow the classical path in the experiment upon e/m and the usual calculation of this quantity from the observations should be correct, as stated by Dr. Eckart. Apparently the only question that could arise would be as to a possible non-classical change in the packet speed u when it leaves the electric field. Since, however, the magnetic field is homogeneous throughout and the

[1] Cf. Page, Phys. Rev. **36,** 1418 (1930).

[2] Cf. G. Neumann, Ann. d. Physik **45,** 529 (1914).

[3] E. H. Kennard, Zeits. f. Physik **44,** 326 (1927).

electric field does not enter into the quantum-mechanical expression for packet speed, it seems safe to assert without detailed calculation that such a change cannot occur.

Professor Page interprets his results as referring to electrons having a certain energy. The "energy of an electron in a magnetic field," as distinguished from the total energy of electron and field, is, however, a complicated question even in classical theory and Page's results require, I think, further analysis before their significance can be properly appreciated.

Apparently no one has published a general formula for the motion of a wave-packet of any type in a general electromagnetic field. The writer has submitted for publication a paper in which this formula is obtained in a simple manner, the result being classical for uniform fields either in non-relativistic theory or for the relativistic electron of Dirac.

E. H. KENNARD

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November 5, 1930

Simple Isotopic Constitution of Caesium

By means of a mass-spectrograph similar to Dempster's, but of greater resolving power, caesium has been found to have but one isotope, within the limits of measurement. This result presents the possibility of a packing fraction of -14.3 compared to -5.3 ± 2 for Xe and I, or as an alternative, an error amounting to 0.077 percent in the accepted determination of the chemical atomic weight 132.81, assuming that the packing effect is similar to that for I and Xe. Aston[1] using photographic recording of the ion beam, likewise observed one isotope only, Cs^{133}. With electrical recording a lower limit may be placed on the relative abundance of any other isotope with respect to Cs^{133}.

If a packing fraction of -5.3, (I and Xe -5.3 ± 2), is taken for Cs^{133} on the $O^{16}=16.000$ scale then the following percentages of single isotopes would be required to give the chemically determined atomic weight 132.81. These amounts are expressed as percentage abundance relative to 132.93 taken as 100 percent.: 13.63 percent of isotope 131.93, 6.36 of 130.93, 4.16 of 129.93 or 3.1 of 128.93. If a lower limit of -7.3 is taken for the packing fraction of Cs^{133} then relative to 132.903 the following percentages of any single isotope are 10.2 of 131.903, 4.87, of 130.903, 3.2 of 129.903 or 2.38 of 128.903. For oxygen = 16.000 on the chemical scale, the percentages of the other isotopes would lie between the above values on the basis of a packing fraction of -5.3, equivalent to -6.55 on the $O^{16}=16.000$ scale. No indication has been obtained of any single one of these possible isotopes being present to even one tenth of the above percentages. The resolving power, $M/\Delta M$, of the mass spectrograph was 200 to 230 for the five best runs with the peak value of the Cs^{133} ion current ranging from 300 to 3600 mm (3×10^{-9} amperes), on the scale of a Compton electrometer with shunting resistances for current measurement. The caesium ions were obtained from a tantalum strip coated with pollucite from Newry, Maine.

Until the packing fraction of caesium is determined directly the source of the discrepancy between the simple isotopic constitution of caesium and the chemical atomic weight cannot be determined. It is, of course, quite possible that the chemical atomic weight is correct and that caesium has an abnormally low packing fraction. It is unfortunate that in the case of Aston's original measurement in 1921 no special accuracy of mass measurement[2] was sought with caesium, even though a packing fraction of -14.3 ($O^{16}=16.000$) was within the range of the mass spectrograph in use at that time.

This work is being extended to barium and strontium at the present time.

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National Research Fellow
Bartol Research Foundation of the Franklin Institute,
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November, 1930

[1] F. W. Aston, Phil. Mag. **42**, 436 (1921).
[2] Reference 1, p. 440.

Problems in Acoustic Interferometry with Gases

In a recent communication to this journal Elias Klein and W. D. Hershberger (Phys. Rev. **36**, 1262, Oct. 1, 1930) point out that the variation of plate current in the Pierce acoustic interferometer with increase in the length of the resonant column of gas is a function not

only of the absorption of the gas but of the circuit constants as well, and that accordingly the deductions of Pielemeier (Phys. Rev., **34,** 1184–1203, Oct. 15, 1929) of ultrasonic absorption coefficients from plate current variations without taking circuit constants into account is probably not justified. Precisely this consideration together with the fact of the nonlinearity of the characteristics of vacuum tubes was the basis of experiments reported by me at the April meeting of the American Physical Society (Phys. Rev. **35,** 1442, June 1, 1930). In these experiments the piezoelectric plate was part of a secondary circuit loosely coupled to a separate oscillator, and the very small (second order) cyclical changes of frequency caused by lengthening the gas column were compensated by adjusting a vernier condenser in the circuit. The quartz plate together with the column of gas was considered as a mechanical system of two degrees of freedom and its effect in the circuit was worked out in terms of circuit and mechanical constants, the frequency being constant. It is thus possible to express the absorption coefficient of the compressional waves in the gas in terms of the decrement of capacity compensation.

Since the time of presenting the above paper much improvement in procedure has been made. To secure data of significance on absorption the source of electrical oscillations must be safeguarded from reaction on it by the acoustic system. Methods have been devised of producing oscillations of constant frequency and of amplifying them so that a secondary system could be excited without disturbing the frequency or the amplitude of the exciting e.m.f. The circuit containing the piezoelectric plate and resonant air column is loosely coupled to the output of the amplifier and variation in current to the crystal electrodes as the gas column is lengthened is measured after the manner of W. G. Cady (Proc. I. R. E. **10,** 83–114, 1922). The theory of this system is easily derived by extending the treatment given by Professor Cady so as to take account of the mechanical action of the gas. The results under these conditions are quite independent of vacuum tube characteristics. The greatest improvement in method has resulted from the use of two piezoelectric plates of nearly the same frequency, one of which is used in a piezoelectric oscillator, the other of which is used in a simple circuit loosely coupled to the amplified output of the oscillator, and serves as a generator of compressional waves in the gas. Under these conditions frequency and amplitude of exciting e.m.f. are constant, considerations of the highest importance in the mathematical treatment.

One result of these measurements is the remarkable precision with which the resonance positions of the reflecting plate may be measured. Much difficulty has been encountered in securing screws of sufficiently small error and of sufficiently good design of mounting to hold their calibrations. Up to the present it is possible under best conditions to obtain values of velocity to one part in twenty thousand. For higher precision a screw system as good as that necessary for ruling an optical diffraction grating would be necessary. Incidentally, it may be remarked that the acoustic interferometer is a most convenient instrument for the calibration of screws. In the frequency limits in which I have so far worked (between 218 and 476 k.c.) I have not been able to detect any variation of velocity with path-length as reported by C. D. Reid (Phys. Rev. **35,** 814–831, April 1, 1930) for lower frequencies. This may be due in part to the fact that the wave-length in gases being small compared with the dimensions of the face of the vibrating crystal, any part which may be played by diffraction is probably negligible. For the purpose of comparison of results with those of Reid, measurements are being made at lower frequencies.

As another result of these experiments I have at no time been able to detect any change of velocity with intensity as reported by W. H. Pielemeier (loc. cit.).

The experiments here outlined has been supported by a grant made in 1926 by the Rumford Committee of the American Academy of Arts and Sciences. This grant was renewed in 1928, but it was only during the spring of this year that active work could be undertaken. I am indebted to Mr. Alfred L. Loomis and to the Naval Research Laboratory for some of the crystals which I have used.

J. C. HUBBARD

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November 6, 1930

Magnetostriction and Magnetic Hysteresis

In a recent paper on the nature of remanence and hysteresis losses in ferromagnetic materials[1] N. S. Akulov professes to prove that the magnetostriction of a single crystal, expressed as a function of its magnetization, is unaffected by the application of mechanical forces. Since my measurements on the magnetostrictions[2] and on the electrical resistance changes[3] accompanying the magnetization of stretched and unstretched permalloy wires seem incompatible with Akulov's conclusion, I have been led to examine his argument in detail. His mistake lies in his separation of each of the strain components (τ_{ij}) into two parts, one of which (ϵ_{ij}) is said to depend *only* upon the mechanical forces, the other (λ_{ij}) *only* upon the magnetization. The assumption that such a separation is possible begs the question at issue.

My experiments, referred to above, and much other evidence of the same sort, make it abundantly clear that the "magnetic" strain components (λ_{ij}) can be set up either by magnetization or by suitable non-isotropic mechanical stresses. These strain components are not, of course, linear functions of the applied forces in either case, since they exhibit saturation phenomena. They are ordinarily ignored in elastic theory and experiment because their limiting values, of the order of 10^{-5}, are nearly negligible in comparison with permissible elastic strains in polycrystalline iron and nickel.

It should also be emphasized that experiment still discloses hysteresis losses and Barkhausen discontinuities in single crystals of iron and nickel, which Akulov regards as inherently free from both of these phenomena. Though the hysteresis losses are much smaller than in polycrystalline iron and nickel, they are, for equal ranges in magnetization, much greater than in polycrystalline perminvar that has never, since its preparation, been subjected to magnetic fields great enough to develop a "wasp-waisted" hysteresis loop. The explanation of perminvar offered by Akulov, which accounts only for the abnormal shape of extensive hysteresis loops, thus fails to account for the principal peculiarity of these materials. His conclusions as to the shapes of internal energy *versus* magnetization curves must, however, be essentially correct, and represent a real advance in the theory of ferromagnetism.

L. W. McKeehan

Sloane Physics Laboratory
Yale University
November 10, 1930

[1] N. S. Akulov, Zeits. f. Physik **64,** 817–829 (1930).

[2] L. W. McKeehan, P. P. Cioffi, Phys. Rev. [2] **28,** 146–157 (1925).

[3] L. W. McKeehan, Phys. Rev. [2] **36,** 948–977 (1930).

Note on the Source of Dielectric Polarization

Dr. J. Hengstenberg has kindly called my attention to an error in my paper on the source of dielectric polarization (Phys. Rev. **36,** 65, 1930) Eq. (1), for the force on an ion in a cubic crystal lattice should read

$$f_e=\frac{K+2}{3}Ee \text{ dynes.}$$

This corrected formula gives, in the case of KCl, values for the fractional change in reflected intensity $\Delta I/I$ almost identical with those calculated by Hengstenberg (Zeits. f. Physik **58,** 345, 1929). My method consists of calculating first, the force on an ion within the lattice which is under electric stress, and then the restraining force constant for an ion from residual ray frequencies. The ratio of these quantities gives the displacement of the ions for any gradient E. Hengstenberg's method consists in assigning one electronic charge to each ion and calculating the necessary displacement of these charges to account for the polarization. If the two theories lead to the same result, as is indicated by the numerical values in the case of KCl, then it should be possible to calculate the dielectric constant from the wave-length of the residual rays λ, the atomic mass m, the distance between adjacent oppositely charged ions r, and known constants. From Hengstenberg's paper

$$P=\frac{K-1}{4\pi}E=\frac{e}{2r^3}\delta r=\frac{e}{r^3}dx$$

whence

$$dx=\frac{(K-1)}{4\pi e}r^3E$$

and my Eq. (3) as corrected

$$\delta=\frac{\lambda^2 e}{4\pi^2 c^2 m}\,\frac{K+2}{3}\,E$$

dx and δ are identical, whence

$$\frac{(K-1)}{4\pi e}\,r^3E=\frac{\lambda^2 e(K+2)}{12\pi^2 c^2 m}\,E$$

and

$$\frac{K-1}{K+2}=\frac{\lambda^2 e^2}{3\pi c^2 m r^3}$$

If m is assumed to be the average mass of the ions of the lattice, then $m=M/2N$ where M is the molecular weight of the compound and N is Avogadro's number.

Then

$$\frac{K-1}{K+2}=\frac{2\lambda^2 e^2 N}{3\pi c^2 r^3 M}=a$$

Whence

$$K=\frac{2a+1}{1-a}$$

Taking the values $N=6.06\times10^{23}$; $e=4.77\times10^{-10}$; $c=3\times10^{10}$

$$a=3.25\times10^{-17}\frac{\lambda^2}{Mr^3}$$

The following table gives the values used in the calculation of K and the result together with observed values of dielectric constant for a number of crystals of the KCl type.

Compound	λ(in μ)	M	r(in A.U.)	a	K calc	K obs
KCl	63.4	74.6	3.14	0.56	4.8	5.0
NaCl	52.0	58.5	2.81	.68	7.4	6.1
AgCl	81.5	143.3	2.77	.71	8.4	11.2
KBr	82.6	119.0	3.30	.52	4.3	5.1
AgBr	112.7	187.8	2.90	.90	28.0	12.2
KI	94.1	166.0	3.53	.39	2.92	5.4
Diamond					1.00	16.5

The fact that these calculations lead to values for the dielectric constant in most cases of the same order of magnitude and in some cases almost identical with those observed, leads one to believe that ionic displacement is an important factor in the polarization in a material of this sort. That this cannot be the only factor however is evident from the values for NaCl and AgBr where ion displacement alone predicts a greater dielectric constant than that actually observed. Further there are non-polar crystals of which diamond is an example, which on this basis should have a dielectric constant of unity instead of the observed value of 16.5. Hence the fraction β of the polarization due to ion displacement lies somewhere between 0 and 1, the value apparently varying from crystal to crystal. The resulting variation in intensity of reflected x-rays would then be for a given field strength, $(\Delta I/I)\propto\beta^2$.

Hengstenberg's experimental results indicate that β lies between 0.8 and 1.4 for his 1900 esu/cm observation and between 1 and 1.2 for his 3000 esu/cm observation. My results indicate that β is probably not more than 0.75 for a rough estimate over a comparatively large number of observations. My experimental values represent averages of ionization currents over long periods of time —a method of observing which tends to eliminate the effect of fluctuations; while those of Hengstenberg are direct readings of a quantity which is difficult to keep constant to 1/10%.

It seems worth while to call to mind in this connection the result of x-ray measurements on electron distribution in crystals of this sort. The results of such measurements indicate that the extra electron of the metal atom does not go over completely to the halogen atom. In other words the probable position of the extra electron is such that part of the time it is associated with the metal atom and part of the time with the halogen atom. This would lead to a value of β less than 1.

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November 5, 1930

A Diophantine Equation Connected with the Hydrogen Spectrum

The wave-length λ corresponding to a line in the hydrogen spectrum is given by Balmer's formula

$$\frac{1}{\lambda}=R\left(\frac{1}{m^2}-\frac{1}{n^2}\right),$$

where R is the Rydberg constant and the integers m and n are the principal quantum numbers. The question then naturally arises whether two different pairs of quantum numbers (m, n) and (m_1, n_1) can correspond to the same wave-length, or in other words, whether the Diophantine equation

$$\frac{1}{m^2}-\frac{1}{n^2}=\frac{1}{m_1^2}-\frac{1}{n_1^2} \qquad (1)$$

has any solutions.

It is readily verified that the formulas

$$\begin{aligned} \rho m &= v(u^2-v^2-w^2)(u^2-v^2+w^2), \\ \rho n &= u(u^2-v^2-w^2)(u^2-v^2+w^2), \\ \rho m_1 &= 2uvw(u^2-v^2-w^2), \\ \rho n_1 &= 2uvw(u^2-v^2+w^2), \end{aligned} \tag{2}$$

where u, v and w are integers and ρ a common divisor of all four numbers to the right, give a solution of (1). Conversely, when any solution of (1) is given, it is expressible in the form (2), since these equations give the following values of the ratios u/v and w/v: $u/v=n/m$, $w/v=n(n_1-m_1)/m_1n_1$.

From any solution of (1), an infinity of others are obtained by multiplying m, n, m_1 and n_1 by any interger; it is therefore of some interest to show that (1) has infinitely many solutions without a common divisor. Let v and w be relative primes, v odd and w even, and w not divisible by 3; making $u=2v$ and $\rho=v$ in (2), we obtain

$$\begin{aligned} m &= (3v^2-w^2)(3v^2+w^2), \\ n &= 2(3v^2-w^2)(3v^2+w^2), \\ m_1 &= 4vw(3v^2-w^2), \\ n_1 &= 4vw(3v^2+w^2), \end{aligned}$$

and these four numbers have no common factor. In fact, m is not divisible by 2, nor has it any factor in common with v or w, so that a common factor of m, n, m_1 and n_1 must be a common divisor of $3v^2-w^2$ and $3v^2+w^2$ or, both these numbers being odd, a common divisor of $3v^2$ and w^2, which is impossible.

We may obviously assume m to be the smallest of the four numbers; to obtain all the solutions of (1) corresponding to a given value of m, we note that since $n \geqq m+1$, it follows from (1) that

$$\frac{1}{m^2}-\frac{1}{(m+1)^2}<\frac{1}{m_1^2},$$

which gives an upper bound for m_1. Transposing n and m_1 in (1), it is seen that the same upper bound applies also to n, and the solution of (1) with m given is thus reduced to a finite number of trials. In this manner it is seem that there is no solution for $m=1$, 2, 3 or 4, and that all solutions with $m \leqq 10$ are those given in the following table, together with those obtained from it by transposing the two middle terms n and m_1 (in the cases where $n \neq m_1$).

m	n	m_1	n_1
5	6	9	90
5	7	7	35
6	8	9	72
7	8	14	56
10	11	22	55
10	11	24	1320
10	12	18	180
10	14	14	70

T. H. GRONWALL

Department of Physics,
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November 17, 1930.

BOOK REVIEWS

The Theory of Approximation. DUNHAM JACKSON. American Mathematical Society Colloquium Publications, Volume XI.

This book contains five short chapters, and constitutes, as the author states in his preface, "a brief essay in a field on which an encyclopedia might be written." In spite of this modest claim the author has assembled in compact yet lucid form a surprising number of fundamental theorems together with complete proofs. With the aid of this book a beginner in the field of approximations may become master of the essential concepts, methods, and results, without extensive reference to the original literature. To a large degree the material contained in the book is the fruit of the author's own extensive investigations in the subject of approximations.

In broad outline the problem which is dealt with throughout the book is the determination of the degree of accuracy by which a given fuction $f(x)$ can be represented by means of a polynomial of assigned degree or by a trigonometric sum of given order of the form

$$a_0+a_1\cos x+a_2\cos 2x+,\cdots,+a_n\cos nx$$
$$+b_1\sin x+b_2\sin 2x+,\cdots,+b_n\sin nx$$

though brief reference is made to approximations using series of more general functions.

Chapter I, entitled "Continuous Functions," deals with the degree of approximation obtainable with a specified number of terms either of a polynomial or of a trigonometric sum for the case in which the given function has suitable properties of continuity. Chapter II, entitled "Discontinuous Functions; Limited Variation; Arithmetic Means;" treats the same problem for the case in which the given function or certain of its derivatives are discontinuous but are of limited variation. It also deals with the degree of convergence of the arithmetic means of a Fourier series. Chapter III treats the degree of approximation obtained by the method of least squares, in which the integral of the square of the error is a minimum, and by the method of least mth powers, in which the mth power of the absolute error is a minimum. The case of weighted approximation is also considered as well as the case of polynomial approximation over an infinite interval. Chapter IV considers the degree of approximation obtainable by means of a trigonometric sum which is determined by the method of trigonometric interpolation. Finally Chapter V, entitled "Introduction to the Geometry of Function Space," brings out interesting geometric interpretations of the formulas of multiple and partial correlation, a subject which is somewhat loosely related to the preceding work on approximation by the principle of Least Squares.

Since the approximate representation of functions plays such an important role in the technique of the mathematical physicist, and since a knowledge of the order of accuracy obtainable in each given case is equally important, this book should prove a valuable aid to physicists as well as to mathematicians.

W. E. MILNE

Allgemeine Physik der Röntgenstrahlen. FRITZ KIRSCHNER, Privatdozent an der Universität, Munchen; comprising Volme 24, Part 1 of the Handbuch der Experimental Physik, edited by (the late) W. Wien and F. Harms. ix+548 pages. Akademische Verlagsgesellschaft m. b. H., Leipzig. Price bound, Rm 55.

Volume 24 of this well-known Handbuch is devoted to x-rays, Part II on X-Ray Spectroscopy having appeared somewhat earlier than the present Part I, which, as the title indicates, deals mainly with the fundamental principles of x-rays and their effects on matter.

The contents of the book can best be given by quoting the titles of its twelve chapters: The Production of X-Rays; High Voltage Sources; Current-Voltage Characteristics of X-Ray Tubes; The Intensity of the Radiation emitted by the X-Ray Tube; The Photoelectric Effect of X-Rays; Scattered (i.e. Compton recoil) Electrons; Characteristic X-Rays and Characteristic Electron emission; Secondary Effects of X-Rays Produced by Photo- and Scattered Electrons;

The Nature of Scattered Radiation; The Intensity of Scattered Radiation; Survey of the Theories of the Scattering of X-Rays; The Determination of X-Ray Wave-lengths by Diffraction and Interference.

With a thoroughness characteristic of the volumes in this series, the author has given a complete survey of each of the above-mentioned subjects. Not only are there copious references to the various articles, but numerous important articles are discussed in detail and very frequently data tables and graphs are reproduced. The discussion is seldom critical, however, and accordingly the reader must usually make his own evaluation of the importance of a given investigation.

Taken in combination with Part II, the present volume places before investigators and students a complete compendium of the more important experimental work which has been done in the field of x-rays. The volumes will be invaluable for both reference and study.

F. K. RICHTMYER

Les Statistiques Quantiques. LEON BRILLOUIN. Two volumes, pp. 404, figs. 26. Les Presses Universitaires de France, 1930. Price 125 francs.

A number of books on quantum mechanics have recently appeared in which the central theme is essentially spectroscopic. Although the development of this field has been most tremendously accelerated since Bohr's treatment of the hydrogen atom, the earliest work on black-body radiation, and some of the newest on the properties of solids, lie in other fields. Professor Brillouin has given a most delightful and stimulating resumé of many of the problems and accomplishments of the quantum theory along these lines. Although these volumes do not purport to be an exhaustive treatise on the subject, they do give a comprehensive treatment of quantum statistics with a wide variety of applications.

The rather classical treatment of black-body radiation is taken over, to a large extent, from the author's previous book and differs from the more common treatment by its emphasis upon the conditions in dispersive media. The discussion of phase, group, energy, and signal velocities is especially valuable at the present time. As is to be expected, the treatment of light quanta has been apparently much influenced by the ideas of deBroglie, with the result that a good deal of space is given to the equations of motion of the protons. A number of very interesting applications of these equations are made in this connection.

In the chapters on thermodynamics and statistics the connection between these two points of view is very nicely made. One could wish, however, that more emphasis had been laid upon the distinctions in point of view between the classical and the quantum theoretical methods of determining probabilities. In particular the work of Schroedinger lends a clarity of idea to the quantum method which is worthy of a good deal of attention. In connection with the discussion of the Fermi-Dirac statistics the applications made by Sommerfeld and Pauli to the electrons in metals are treated with a clear indication as to just what features are characteristic of the newer statistics.

In continuation of the subject of electrons in metals the first half of the second volume is devoted to the problem of the quantum mechanical evaluation of the mean free path. Professor Brillouin evidently does not consider the simpler methods as very significant, but he gives a thorough treatment of the more elaborate calculations of Bloch. He also gives an excellent presentation of the problem of an electron in a sinusoidal field of force. The remainder of the second volume is occupied by a discussion of the statistical treatment of the electron distribution in an atom, and of the distribution of atoms among various quantized states. There is also a very valuable and exhaustive bibliography.

To one who wishes an acquaintance with the wide applicability of quantum theory outside the field of spectroscopy, or to one who is interested in the possibilities of a satisfactory theory of solid bodies, these two volumes will be a most valuable aid.

W. V. HOUSTON